UNIVERSITY OF EDINBURGH.

THE ACTION OF ELECTROLYTES ON COLLOIDAL PRUSSIAN BLUE.

by

WILLIAM TAYLOR, B.Sc.

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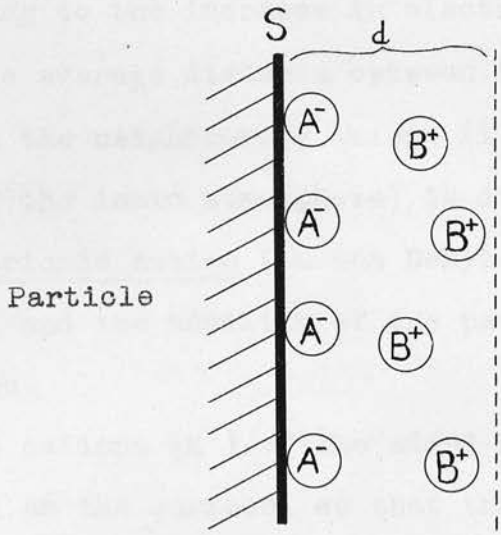
C O N T E N T S.

INTRODUCTION.

It is commonly supposed that the stability of a lyophobic sol depends essentially upon the electrical conditions at the surfaces of the colloidal particles. Undoubtedly there exists, in general, a parallelism between the manner in which electrolytes influence the speed of migration of the particles in an electric field on the one hand and their coagulating action on the other. Thus for any particular sol, the more powerful an electrolyte is as a coagulant, the smaller is the concentration required to reduce the cataphoretic velocity by a given amount. Again, where with increasing concentration of electrolyte the migration is first depressed to zero and then increased again, but in the opposite direction, the stability of the sol passes through a minimum at the iso-electric point.

In many instances the electrokinetic behaviour of a particle may be attributed to the existence of an electric charge on the surface, due to either (1) adsorption of ions or (2) dissociation of the surface molecules of the particle. When the charge is negative, for example, the former case may be represented as in the accompanying diagram.

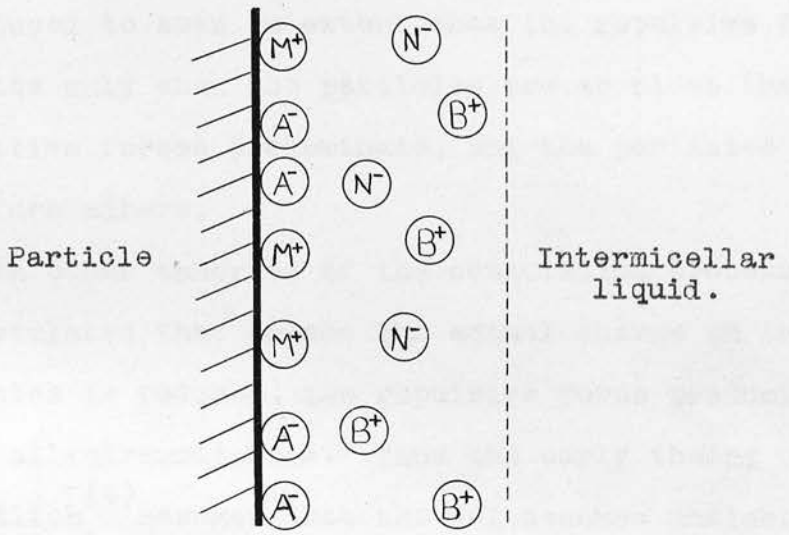


The surface (S) of the particles adsorbs the anions (A^-) of some particular electrolyte (AB) and these hold an equivalent amount of cations (B^+) in their neighbourhood. An electrical 'double layer' is thus formed, the ions composing the inner layer being fixed at the surface of the particle, while those of the outer layer are mobile, having a range of movement (d) limited by the electrostatic attraction of the inner layer and constituting an 'ionic atmosphere' round the particle. It is obvious that a similar state of affairs exists when the charge arises through 'surface dissociation'.

The decrease in the speed of cataphoresis produced by the introduction of an electrolyte (MN) having no ion in common with AB , is conceivably due to one or more of the following three effects.

(a) Owing to the increase in electrolyte concentration, the average distance between the absorbed ions (A^-) and the neighbouring anions (i.e. the mean 'thickness' of the ionic atmosphere) is diminished. Hence the interionic action (in the Debye-Hückel sense) increases, and the mobility of the particle consequently decreases.

(b) The cations (M^+) of the added electrolyte may be adsorbed on the surface, so that the net density of charge is reduced, thus:-



(c) The cations (M^+) of the added electrolyte may form undissociated molecules, or associated ion-pairs, with the anions (A^-) of the adsorbed electrolyte, again producing a decrease in the charge.

In accordance with the foregoing considerations, the coagulating action of electrolytes has been ascribed either to decrease in the thickness of the double layer, or to decrease in the surface density of the charge.

According to the theories of Kruyt[1], Verwey[2], and Hamaker[3], a repulsive force comes into play when two particles approach so closely that their ionic atmospheres meet. In the case of a stable sol the thickness of the atmospheres is such that the particles cannot approach closely enough for the attractive forces between them to overcome this repulsive force. In the presence of a sufficiently high concentration of electrolyte, however, the thickness of the atmospheres is reduced to such an extent that the repulsive force operates only when the particles are so close that the attractive forces predominate, and the particles therefore adhere.

In other theories of the coagulation process it is postulated that unless the actual charge on the particles is reduced, the repulsive force predominates under all circumstances. Thus the early theory of Freundlich[4] assumes that the sol becomes unstable when the charge is reduced to a certain value by adsorption of the oppositely charged ion of the coagulating electrolyte (see (b) above). On this view, the same amount of this ion should be taken up by the particles, irrespective of the nature of the coagulant.

(1) Kruyt, "Colloids" (New York), 1927, p.66; Verwey and Kruyt, Zeitschr. phys.Chem.,A.167, 312 (1934).
(2) Verwey and Kruyt, loc. cit.; Verwey, Chem. Reviews, 16, 363, (1935).
(3) Hamaker, Rec. Trav. Chim., 55, 1015, (1936); ibid, 56 3, (1937).
(4) Freundlich and Gann, Kolloidchem. Beih. 8 127,(1916).

The work of Freundlich, Joachimsohn and Ettisch[1], Weiser,[2] and others[3] however indicates that the amount of ion adsorbed is not necessarily a constant.

An alternative hypothesis is, of course, that coagulation is due to diminution of the charge through the formation of undissociated molecules (or associated ion-pairs) between the ions constituting the inner part of the original double layer, and the oppositely-charged ions of the coagulant (see (c) above).[4]

No theory advanced up to the present has been able to provide an adequate interpretation of one of the most striking features of coagulation, namely the differences between the coagulating powers of the various electrolytes. Some recent investigations, however have indicated that study of the process of 'ionic interchange' ('base exchange' or exchange adsorption') may give valuable information in regard to this problem. The process consists in the replacement of some or all of the ions constituting the original outer part/

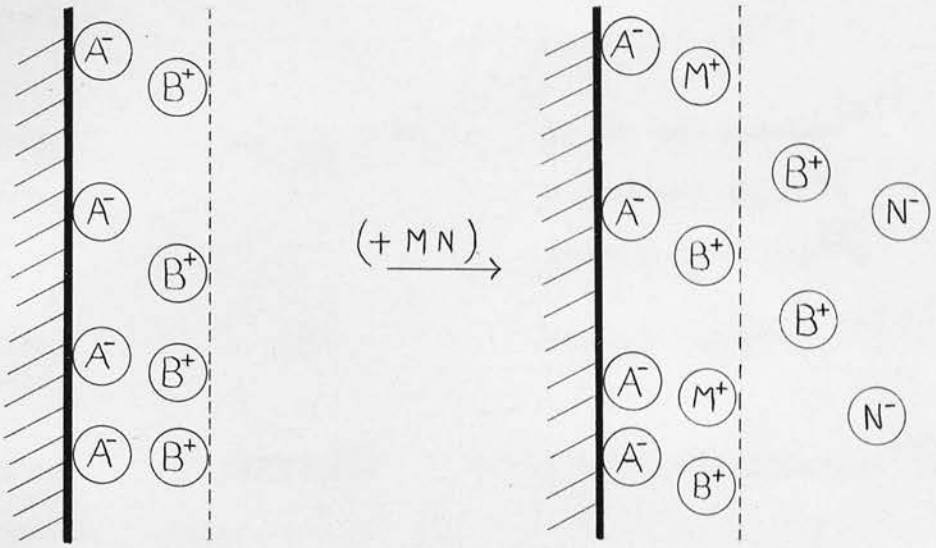
(1) Freundlich, Joachimsohn and Ettisch, Zeitschr. phys. Chem., 141A 249, (1929.

(2) Weiser, Article on 'Adsorption by Precipitates' in Alexander's "Colloid Chemistry" (New York), Vol.I p.600, (1926).

(3) See, for example, Bolam and Bowden, J.C.S. 2684, (1932).

(4) Pauli and Valko, Elektrochemie der Kolloide (Vienna), 1929:
McBain and McClatchie, J.Amer.Chem.Soc.55 1315,(1933)
Usher, Trans. Faraday Soc., 21, 406, (1925-26).
Pennycuick,J.C.S., 618, (1929).
Bassett and Durrant, J.C.S., 2946, (1931).

part of the double layer by oppositely-charged ions of the coagulating electrolyte, as shown in the following diagram.



When, in the case of a negative sol, the stabilising electrolyte (AB) is an acid, the interchange results in liberation of hydrogen ions from the neighbourhood of the particle, and their appearance in the intermicellar liquid. Estimation of the concentration of acid in the intermicellar liquid (or supernatant liquid, if complete coagulation occurs) thus gives a direct measure of the degree to which interchange has occurred. The liberation of hydrogen ions by ionic interchange has been studied in the following instances.

Sol	Stabilising Acid.	Investigators.
Arsenious sulphide	H_2S	Weiser and Gray[1].
		Rabinowitch[2].
Sulphur	Polythionic Acids	Bolam and Bowden[3].
		Bolam and Muir[4].
		Weiser and Gray[5].
Silver iodide	HI	Verwey and Kruyt[6].
Cupric ferro-cyanine	$H_4Fe(CN)_6$	Weiser and Milligan[7].
Stearic Acid.	Stearic Acid	Bolam and Duncan[8].

(1) Weiser and Gray, J. phys. Chem., 36, 2796, (1932).

(2) Rabinowitch, Z. physik. Chem., 116, 97, (1925).

(3) Bolam and Bowden, J.C.S., 2684, (1932).

(4) Bolam and Muir, J.C.S., 1022, (1933): J.C.S., 754, (1934).

(5) Weiser and Gray, J. phys. Chem., 39, 1163, (1935).

(6) Verwey and Kruyt, Z. physik. Chem., 167A, 312, (1934).

(7) Weiser and Milligan, J. phys. Chem., J. phys. Chem., 40, 1071, (1936).

(8) Bolam and Duncan, J.C.S., 1317, (1936).

The results, without exception, show that the smaller the concentration of salt required to produce a given degree of coagulation, the greater is the degree of ionic interchange produced by a given concentration of the salt. Thus when a series of salts are arranged in sequence according to the tendency of the cation to liberate hydrogen ion, the same order is obtained as when the salts are arranged according to their coagulating powers.

The data obtained by Bolam, Bowden and Muir (loc. cit. p. 7) for sulphur and stearic acid sols, indicates that a close connection exists between coagulating power and tendency to ionic interchange. It was found that the same amount of hydrogen ion was liberated by all the salts examined, when present at the respective concentrations necessary to produce a given degree of instability. This phenomenon is inexplicable on the basis of the theories of Kruyt, Verwey, and Hamakers (loc. cit. p. 4), at least in their present form, which assumes simple ionic interaction of the Debye-Hückel type. It is clear that strong specific forces are involved, but whether they result in the formation of undissociated molecules or ion pairs (i.e. the destruction of the ionic atmosphere) or simply to decrease in the thickness of the ionic atmosphere/

atmosphere (as suggested by Weiser (loc.cit. p. 7) is difficult to decide. In any case it would appear that observations on ionic interchange may be highly significant for a comprehensive theory of the mechanism of coagulation (cf. Verwey, loc. cit. p. 4).

It is obviously of importance to ascertain if constancy in the degree of ionic interchange at the coagulation-point is a general phenomenon, and the present investigation was initiated with the object of determining whether colloidal prussian blue resembled sulphur and stearic acid in this respect. As will be shown in the sequel, the situation in the case of the particular sols examined (prepared by peptising prussian blue with oxalic acid) is complicated by the liberation of acid by processes other than ionic interchange of the type described in the foregoing. Although, owing to this complication, it was not possible to prove definitely that ionic interchange is a constant at the coagulation point, the data obtained are not inconsistent with the assumption that this is actually the case.

EXPERIMENTAL.

MATERIALS AND APPARATUS.

CHEMICAL REAGENTS.

With the exception of lithium chloride all the salts, acids and alkalies employed throughout the research were of A.R. quality. Preliminary work showed that it was necessary to reduce the alkalinity of the lithium chloride solutions prepared from the commercial sample. Two recrystallisations from water sufficed for the preparation of a satisfactory solution. Lead chloride was prepared[1] by dissolving A.R. lead nitrate in water and adding excess of A.R. hydrochloric acid. The precipitate was washed thoroughly in ice-cold water until free from nitrate. The salt was re-crystallised twice from water.

Hydroferrocyanic acid was prepared from A.R. potassium ferrocyanide and A.R. hydrochloric acid by the method used by Weiser and Milligan[2]. The white solid acid was twice recrystallised from absolute alcohol and absolute ether and finally dried over concentrated sulphuric acid in an evacuated desiccator. The product was stable in the absence of moisture.

Quinhydrone/

(1) Baxter and Glover. J.A.C.S. 37 1050 1915.

(2) J. Phys.Chem. 40 1071, 1936.

Quinhydrone, for the electrical measurements, was prepared by the method of Billman and Lund,[3] washed with ice cold water until free from acid, dried over calcium chloride in an evacuated desiccator and kept in a glass stoppered bottle.

All solutions were made up with water of specific conductivity 1.6×10^{-6} mho. and stored in Jena glass bottles. The concentrations of the chloride solutions used in the quantitative work were checked by means of conductivity measurements, use being made of appropriate data from the International Critical Tables (VI, 236)

VOLUMETRIC APPARATUS.

As the preparation of the sols was a long and laborious process, it was desirable to use as small a quantity of sol for each experiment as was consistent with the accuracy required. It was necessary to ensure that the volumes of sol and solution taken could be accurately measured and reproduced. Actually two pipettes were employed, one delivering on the average 2.004 mls and the other 2.995 mls. Table I shows that the error in the measurement of volume did not exceed $\pm$ 0.1%.

(3) Ann. de Chem. 15 128 1928.

TABLE I.

2 ml. pipette.

Temp. 17°C.

Weight of water delivered (grams)	Mean Weight	Divergence from mean.
2.0008		+ 0.0015
1.9988		- 0.0005
	1.9993	
1.9984		- 0.0009
1.9991		- 0.0002

3 ml. pipette.

Temp. 18°C.

Weight of water delivered (grams)	Mean Weight.	Divergence from mean.
2.9890		+ 0.0011
2.9864		- 0.0015
2.9888	2.9879	+ 0.0009
2.9889		+ 0.0010
2.9866		- 0.0013

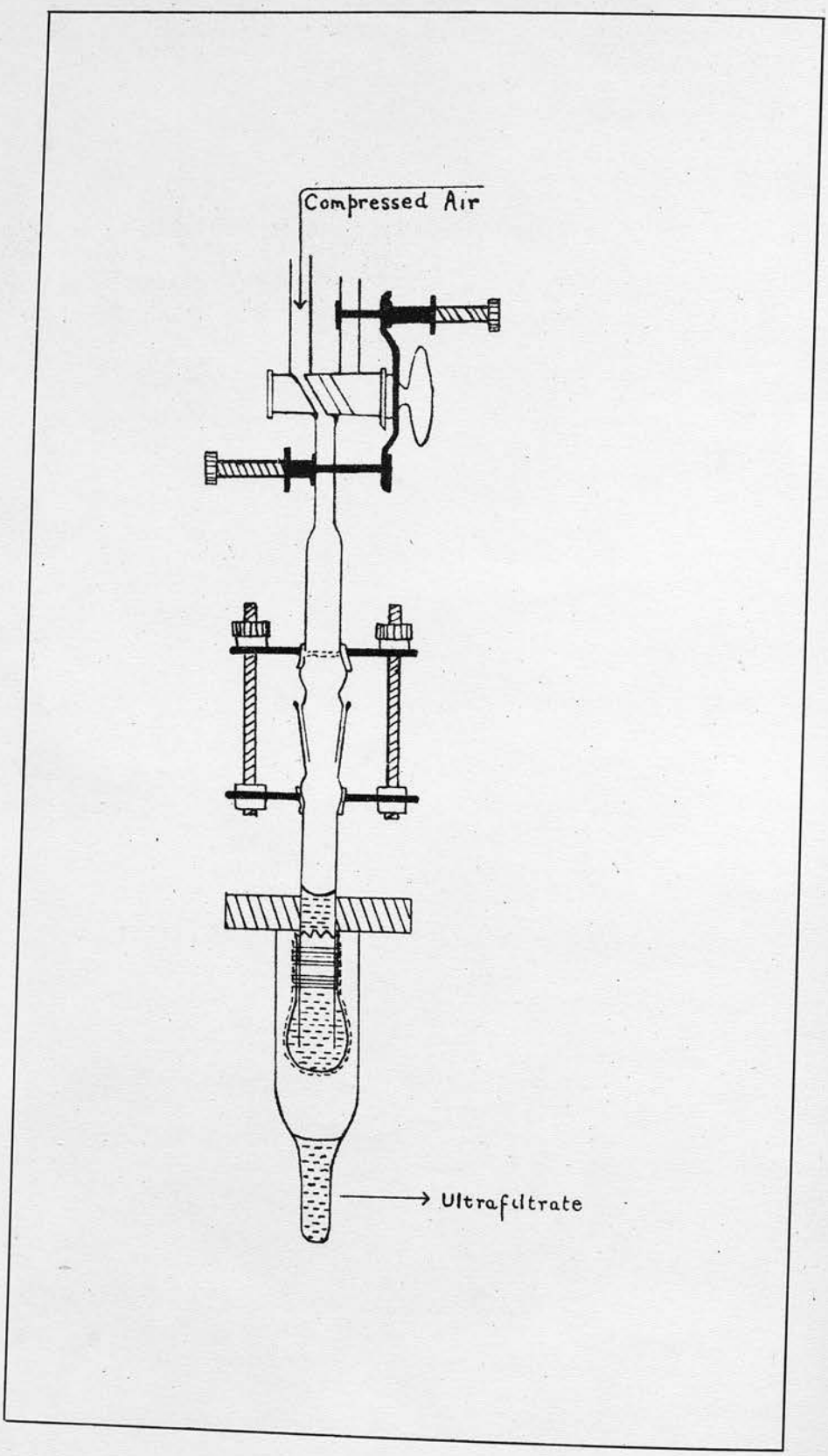
CONDUCTIVITY MEASUREMENTS.

The conductivity apparatus comprised a calibrated three metre drum bridge, a Gambrell resistance box Class A , and a buzzer with telephone for the detection of the null point. The conductivity cell was constructed of pyrex glass and was closed with a ground glass cap to exclude atmospheric impurities. The cell was immersed in a gas heated thermostat maintained at $25^{\circ} \pm 0.05^{\circ}$ C. The maximum error in the determination of the mull point did not exceed $\pm$ 0.2%.

GLASS APPARATUS.

Except in a very few instances, the glass-ware used in the course of the research was constructed of either Pyrex or Jena glass. Before use pipettes, test-tubes, flasks, bottles, beakers etc., were always treated with concentrated sodium hydroxide and hydrochloric acid, thoroughly washed with distilled water, steamed out for at least half an hour, and finally dried in an oven.

Fig 1.



ULTRAFILTRATION.

Two types of ultrafilters were used (1) Low pressure apparatus for the ultrafiltration of small quantities of liquid (up to 5 mls) and (2) High pressure apparatus designed for larger volumes (up to 150 mls).

Low Pressure Ultrafilter.

This apparatus has been described by Bolam and Bowden[1] (see fig. 1). A small bag of cellophane No. 300 was tightly bound over the end of a glass tube with linen thread, and a thimble of welded platinum gauze to support the membrane slipped over the bag and also bound by linen thread to the glass tube. The liquid to be ultrafiltered was pipetted into this tube, which was connected to the rest of the apparatus by a ground glass joint. A pressure of two atmospheres was applied to the liquid by means of a mercury column. Since the area of the membrane was small and the applied pressure low, ultrafiltration was an exceedingly slow operation, 2 mls. liquid passing through in 3 - 4 hours. To minimise evaporation from the filtrate, the pyrex glass receiver was arranged so as to enclose the membrane and platinum gauze, being held in position by a single bore rubber stopper through which the glass tube was passed.

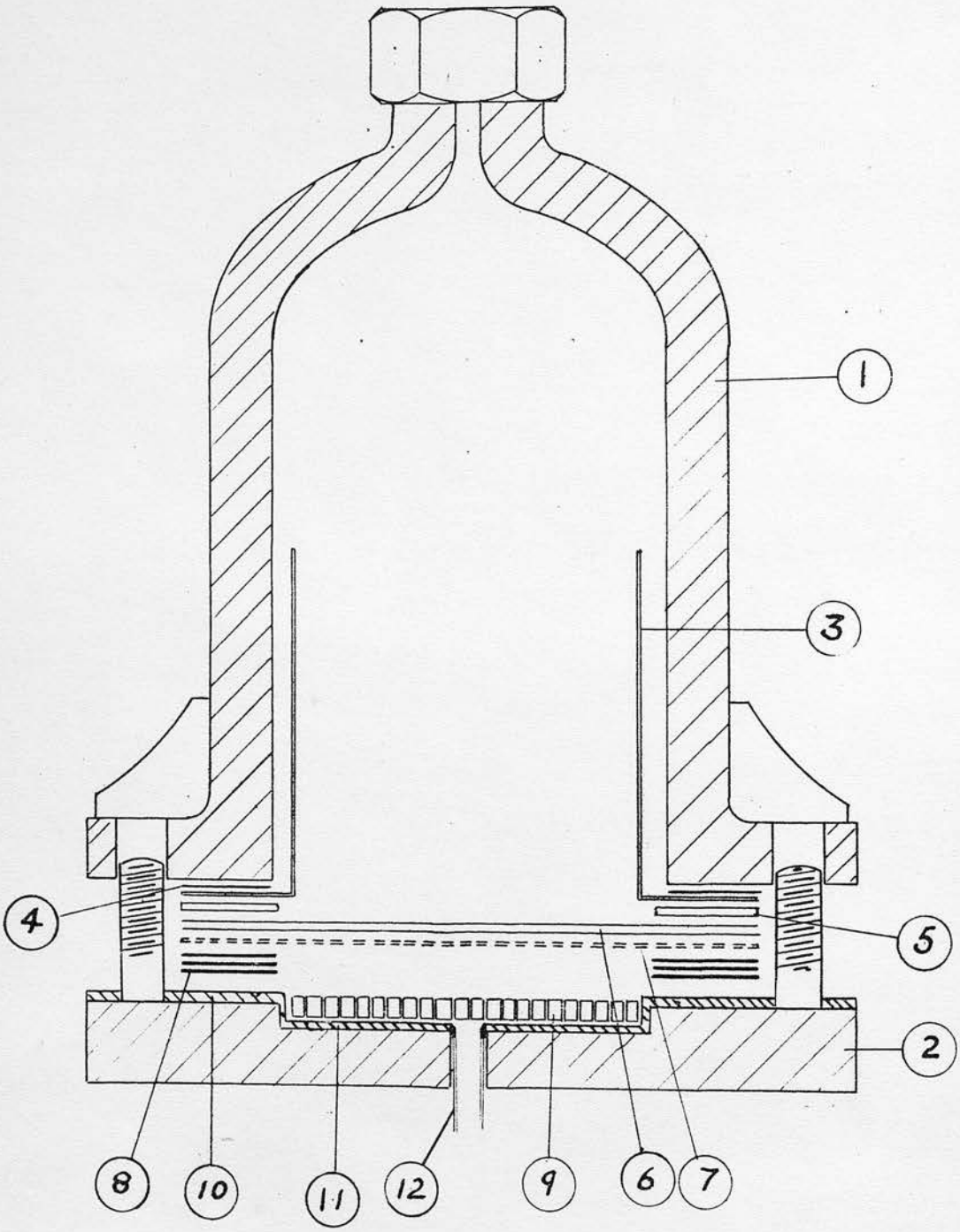
(1) J.C.S. 2690, 1932.

To determine if the ultrafiltration produced any change in concentration, the conductivities of solutions of lithium and potassium chloride were measured before and after filtration. The data showed (Table II) that the concentration increased by about 1%.

TABLE II.

Solution.	Specific Conductivity k (mho x 10^3)	Change in k (x 10^3).
0.04 M LiCl	3.810	-
"	3.814	-
do. ultrafiltered	3.860	+ 0.044
" "	3.840	+ 0.042
0.04 M KCl	5.374	-
"	5.379	-
do. ultrafiltered	5.391	+ 0.015
" "	5.481	+ 0.105
" "	5.405	+ 0.029

Fig. 2.



High Pressure Ultrafilter.

The apparatus used (see fig. 2) was a modified form of the well known type supplied by Vereinigung Göttinger Werke, Göttingen. It consisted essentially of a phosphor bronze dome (1) of circular cross-section which served as the filter chamber or reservoir and a circular bronze base plate (2), the membrane support. The filtering medium with its supporting structures was interposed between those two parts which were then bolted together by a ring of nine bolts and nuts, a gas and liquid tight joint to withstand high pressure being obtained by rubber and cellophane washers.

Two discs (6) of cellophane (colourless No. 300) were used as membranes and in order to prevent rupture on the application of pressure, they were supported by a platinum gauze (7) (mesh 48) which was supported in turn by a perforated celluloid disc (9) inserted in the base plate. To protect the gauze from shearing stresses on bolting the parts of the apparatus together, three thick cellophane washers (No. 2400) were inserted between it and the base plate. A protective coating of $\frac{1}{8}$" celluloid (10) and (11) was cemented on the base plate and the liquid, after passing through the membranes and the perforated disc, was conducted down/

down channels cut in (11) and withdrawn from the apparatus by the pyrex glass tube (12) which was cemented into the celluloid. A cylinder of celluloid (3) was cemented into a thick celluloid ring, which fitted over the studs, thus providing a complete sheath inside the dome. A gas tight joint was obtained by means of a thick cellophane ring (4) inserted between the base of the dome and the celluloid ring, a rubber washer under the latter acting as a liquid tight joint and preventing rupture of the membranes.

In an actual experiment, the apparatus was assembled as shown in the diagram. The solution to be ultrafiltered was introduced at the top of the dome which was then closed by means of a nut carrying a pressure gauge and needle valve, to which was attached a flexible copper pipe from a high pressure nitrogen gas cylinder. The normal working pressure, controlled by the needle valve, was from 50-60 kilos. per sq. cm., and under these conditions the duration of the filtration was uniformly 2½ hours for 50 mls of liquid. The ultrafiltrates were collected in pyrex flasks and were perfectly clear when protected from the action of light. On dismantling the apparatus after a filtration experiment, the coagulum was found as a solid cake on the membrane and was immediately available for analysis.

Owing to the high acid content of the sols and the mechanical forces involved in assembling the apparatus, the internal surface of the filter was a continual source of trouble during the preliminary work. Surfaces

of/

of silver and platinum were tried out but after a short period of use, the films broke down exposing the bronze surface which interacted with the solutions. Finally celluloid was used in the manner described above, which completely eliminated the possibility of contamination of the solutions from interaction with metallic surfaces.

MEASUREMENT OF ELECTROMOTIVE FORCE.

The low concentrations of acid liberated by the action of salts upon the dialysed sols were estimated electrometrically by means of the glass electrode, the complete cell being:-

Hg	Hg_2Cl_2, (Solid)	KCl 3.5 M	KCl 3.5 M	Buffer or 'test' solution	Glass membrane	HCl, quinhydrone 0.1M (solid)	Pt. (polished)

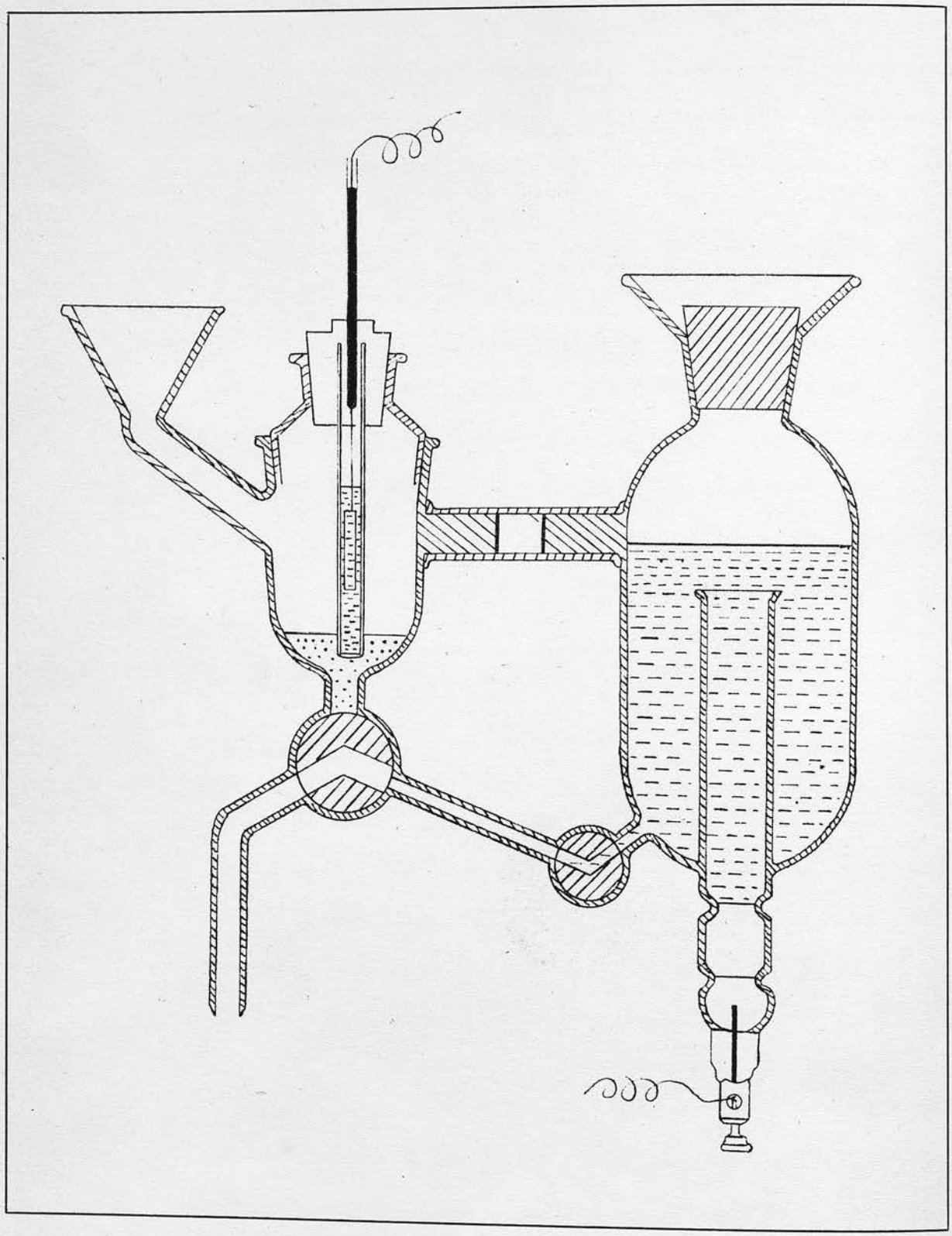
The glass electrodes were of the form described by MacInnes and Dole[1]. An extremely thin membrane of high conductivity glass was sealed over the end of a glass tube ($\frac{3}{16}$th bore), the membranes being made from glass of the formula recommended by Harrison[2] and supplied by C. Dixon and Co., London. The tube was filled with a 0.1 N solution of hydrochloric acid saturated with quinhydrone, into which a strip of polished platinum was dipped[3]. Evaporation from the/

(1) Ind. Eng. Chem. (Anal.) 1, 57, (1929): J.A.C.S. 52, 29, (1930.)

(2) J.C.S. 1528, (1930).

(3) Morton. J. Sc. Inst. 7, 187, (1930).

Fig. 3.



the solution of quinhydrone and hydrochloric acid was prevented by closing the mouth of the tube with a rubber stopper. When not in use, the electrode was kept immersed in a buffer solution.

The remainder of the cell, including the calomel electrode, was of the type designed by Morton and was supplied by the Cambridge Instrument Co. The cell system (shown in fig. 3) had the following advantages in respect to the present work.

(1) Only three to four mls of solution were necessary for a determination.

(2) Contamination by diffusion of potassium chloride from the bridge into the glass electrode half-cell was reduced to very small dimensions.

(3) The test vessel could be easily flushed out by means of the special three-way stop-cock.

For experiments on Sol C and Sol D, the cell was set up in a constant temperature room maintained at $14^{\circ} \pm 0.5^{\circ}C$, and for those on Sol E and Sol F it was enclosed in an air thermostat maintained at $18^{\circ} \pm 0.5^{\circ}C$ (by electrical regulation). In the latter case the calomel and glass electrodes were fixed to electrically insulated racks and the leads connected to shielded terminals held by amberite plugs set in the wall of the thermostat.

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The e.m.f. was measured by means of an electrometer valve potentiometer supplied by the Cambridge Instrument Company. The instrument was found to be sensitive to within about 0.2 millivolt.

The glass electrode was tested at 14°C by means of the following buffer solutions, the pH values of which are accurately known.

(a) Equal volumes of 0.1 M disodium hydrogen citrate and 0.1 M hydrochloric acid[1].

(b) 0.1 M disodium hydrogen citrate.

(c) $\frac{M}{20}$ potassium hydrogen phthalate.[2]

(d) $\frac{M}{20}$ sodium borate.

The data are given in Table III and it will be seen from the constancy of the figures in the last column that the behaviour of the electrode was normal[3].

The e.m.f. given by the buffer solution $\frac{M}{20}$ potassium hydrogen phthalate was determined daily in order to allow for variation in the behaviour of the glass electrode. All readings were made 20 minutes after the cell was assembled, by which time the e.m.f. had usually attained a constant volume. In most cases the amount of 'test' solution available was 8 mls and the estimation was carried out in duplicate with the same solution.

The/

(1) Sorensen: Biochem. Z. 21, 131, (1909).
(2) Clark. J. Biol. Chem. 25, 479, (1916).
(3) Hughes. J.C.S. 491, (1928).
MacInnes and Dole. J. Am. C.S. 53 3315 (1931).
Davidson. Shirley Instit. Mem. 12 4, 1933.

The concentration of acid was deduced from the quantity $E = E - E'$, where E = e.m.f. given by the 'test' solution and E' = e.m.f. given by $\frac{M}{20}$ potassium hydrogen phthalate (see p. 40).

Values of pH (see Table XII) were calculated from the relation

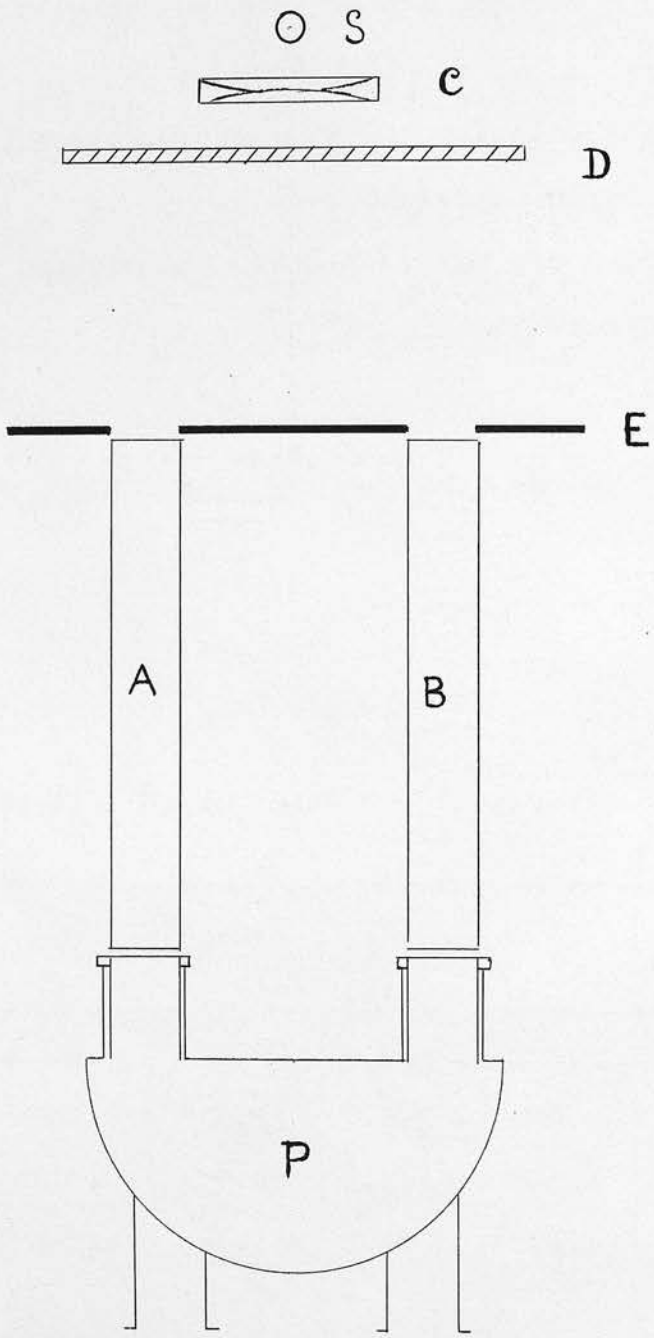
$$pH = 3.97 - \frac{E_{14^o} - E'_{14^o}}{0.0569}$$

TABLE III.

Calibration of the Glass Electrode.

Buffer Solution	pH	E.m.f. (millivolts)	E.m.f.	pH	$\frac{\text{E.m.f.}}{\text{pH}}$
a	3.692	+ 239.8	-	-	-
b	3.97	+ 224.0	15.8	0.278	56.8
c	4.958	+ 167.7	56.3	0.988	56.9
d	9.20	- 73.7	241.4	4.242	56.9

Fig. 4.



COLORIMETRIC MEASUREMENTS.

The procedure adopted in determining the coagulation values of the various salts involved the estimation of the intensity of the colour in dilute sols of prussian blue. A diagram of the apparatus employed for this purpose is given in Fig 4 . A and B were two 10 cm. polarimeter tubes mounted on special V shaped supports, adjustable for height and direction. The light from a 60 watt Osram bulb (S) passed through the condenser (C), the ground glass plate (D), into A and B through apertures in the screen (E) . The intensities of the beams of light emerging from A and B were compared by means of the Pulfrich photometer (P).

The tube B was filled with distilled water and the size of the corresponding aperture in the photometer kept at the same value for every measurement. An actual estimation was carried out as follows. The tube A was first filled with distilled water and its position adjusted so that the two halves of the photometer field were equally illuminated when the size of the photometer aperture corresponding to tube A was such as to give a reading of 50 on the appropriate dial. The liquid under examination was now placed in A and the dial reading x obtained for uniform illumination of the photometer field under these/

these conditions. Preliminary experiments showed that the amount of absorption was directly proportional to the concentration of prussian blue in accordance with Beer's law. Hence the value of the difference (x - 50) could be taken as a direct measure of the amount of prussian blue present in the liquid, provided the average size of the particles was the same in the systems under comparison.

PROCEDURE AND DATA.

PREPARATION OF PRUSSIAN BLUE SOLS.

All the sols studied in the course of this investigation were prepared from precipitated prussian blue, obtained by the interaction of potassium ferrocyanide with excess of ferric chloride. A solution containing two grams of potassium ferrocyanide in 100 mls of water was slowly run into a solution of two grams of ferric chloride in 100 mls of water, with continuous stirring. After some hours the prussian blue settled out and the supernatant liquid was decanted off. The precipitate was washed with distilled water by decantation from seven to ten times, then filtered off and further washed until the filtrate showed no opalescence with silver nitrate. Owing to the character of the precipitate, filtration was very slow and it was found convenient to restrict the quantity of blue precipitated at any one time to that produced by the above mentioned quantities of reagents.

Sols A and B (undialysed)

To prepare the sol , six portions of the prussian blue were put together and peptised by shaking with 500 mls. water containing ten grams of oxalic acid. To remove any material present as a coarse suspension, the sol was filtered through a Jena fritted glass filter.* The sols were stored in Jena glass bottles and protected from the action of light.

* Büchner type; porosity 4.

Sols C, D, and E (dialysed)

During the course of the research it was found necessary to reduce the high concentration of acid present in the intermicellar liquid of the sols when prepared as described above. A large proportion of the acid was removed by ultrafiltering the undialysed sol by means of a high pressure ultrafilter (see p. 18). The prussian blue was retained by the cellophane membrane in the form of a solid cake which was found to be readily repeptised by treatment with distilled water. Generally about 300 mls. of undialysed sol were ultrafiltered in several portions, the coagulum from each portion being peptised in the minimum amount of water - in order to maintain a high concentration of prussian blue in the final sol. The acid content was still further reduced by dialysing the sol for a period of seven days (eleven days in case of sol E), in collodion bags immersed in running distilled water.
The sols were stored in Jena glass bottles and precautions were taken to protect them from the action of light.

Sols prepared in this manner were very stable and no sediment appeared during the period of investigation.

Sol F was prepared from sol E by the addition of pure hydroferrocyanic acid (see p. 10). A quantity of hydroferrocyanic acid was weighed on a micro balance and/

and added directly to a measured volume of sol E. Thus the concentration of prussian blue in sol F was the same as in sol E. Actually 0.007075 gms. $H_4Fe(CN)_6$ were dissolved in 67.73 mls. sol E , so that the gross concentration of the $H_4Fe(CN)_6$ was 0.001935 N.

ANALYSIS OF THE COAGULUM (SOLS A and B).

The following method was used to determine the alkali content of the coagula produced by the addition of various salts. Twenty-five mls. of a standard salt solution were mixed with twenty-five mls. of sol A in a 100 ml. conical pyrex flask. The contents of the flask were gently shaken, allowed to stand for fifteen minutes, and then transferred to the high pressure ultrafilter. A little of the coagulated prussian blue always adhered to the sides of the flask but its weight proved to be a negligible fraction of the total. After filtration had been completed, the top layer of cellophane with its adherent coat of prussian blue, was transferred to a platinum basin and the cellophane incinerated in presence of the coagulum by means of a small bunsen flame. The temperature was now gradually raised and finally the contents of the basin were ignited for thirty minutes with a full Méker flame.

The/

The residue consisted mainly of red Fe_2O_3 , together with a small amount of alkali carbonate. The ferric oxide was ground to a powder with a platinum rod and the alkali extracted by decantation and washing with hot distilled water. The ferric oxide was removed by filtering through a Jena fritted glass filter (Büchner type; porosity 4), preliminary experiments having shown that some of the oxide was too finely divided to be retained even by Schleicher and Schüll's Blue-band filter paper. The ferric oxide was washed until the filtrate was neutral to phenol red. The large volume (250-300 mls.) of liquid obtained was subsequently reduced to 100 mls. by evaporation on the steam bath.

The alkali content of the filtrate was determined by back-titration, using $\frac{N}{100}$ HCl and $\frac{N}{100}$ NaOH , and phenol red as indicator. An accurately measured excess of HCl (19.99 mls.) was added to the filtrate and the solution boiled for ten minutes to free it from CO_2. The hot solution was then titrated with the carbonate-free NaOH. Since the solutions were dilute, it was found necessary to determine the end-point by reference to colour standards.

In order to determine whether there was any alkali present in the original prussian blue, a mixture of twenty-five mls. sol + twenty-five mls. H_2O was ultra-filtered/

ultrafiltered and the solid residue subjected to the above treatment. The volume of NaOH used in the back titration differed by only 0.02 ml. from that required for direct titration of the added HCl. Hence the solution obtained by extracting the residue left after ignition of the prussian blue was neutral, which showed that no alkali was present in the original prussian blue.

The results of the analyses are given in Tables IV and V .

ANALYSIS OF THE ULTRAFILTRATE.

The presence of ferrocyanide ion in the ultrafiltrates from undialysed sols was indicated by the following observations. (a) With ferric chloride solution a deep blue coloration (formation of prussian blue) was immediately produced. (b) A white precipitate was formed on the addition of ferrous sulphate solution. When this precipitate was filtered off, washed with distilled water, and kept exposed to the light, the colour changed, through green to blue (formation of prussian blue). (c) On the addition of silver nitrate solution, a pale brown precipitate appeared. This was treated with dilute nitric acid (to eliminate silver oxalate) and then with ammonia solution/

solution (to eliminate silver ferricyanide, if present). A white residue remained which proved to be silver ferrocyanide since when treated with concentrated nitric acid, it was converted into a dark brown substance (formation of silver ferricyanide) which dissolved in ammonia solution, and was reprecipitated on acidification with dilute nitric acid.

The absence of ferricyanide ion was established as follows. (d) After the silver precipitate had been treated with ammonia solution, as described above under (c), the solution was acidified with dilute nitric acid. No precipitate appeared, showing that the ultrafiltrate did not contain ferricyanide ion. This, if present, would have been precipitated as silver ferricyanide in the first instance and dissolved out by the ammonia solution. (e) Zinc nitrate gave a white precipitate with the ultrafiltrate (zinc ferricyanide is orange).

The ultrafiltrate gave no red coloration with potassium thiocyanate, but a blue coloration was produced with potassium ferrocyanide. This indicated the presence of ferrioxalate ion, since the same behaviour was shown by a solution containing potassium ferrioxalate (see p. 41) with excess of oxalic acid, and Abegg[(1)] states that solutions of ferrioxalates give the reactions/

(1) Abegg 'Handb. d. anorg. Chem., Bd.IV, 3A btlg, 2 Tl, B380.

reactions for ferric ion, with the exception of the coloration with thiocyanate.

The foregoing remarks apply to an ultrafiltrate which was fresh and protected from the action of light. under these conditions the filtrate was quite clear, being greenish-yellow in colour. If the filtrate was exposed to bright light, a greenish-white precipitate quickly appeared. This gradually increased in bulk and deepened in colour, becoming ultimately dark blue. Hydrogen cyanide was also produced. The liquid was finally quite colourless. A similar process occurred in the dark, but much more slowly.

These changes were undoubtedly due at least in part to the decomposition of the ferrocyanic acid to give hydrogen cyanide and ferrous ferrocyanide. $HFe^{iii}Fe^{ii}(CN)_6$, the latter being oxidised to prussian blue by the oxygen of the atmosphere(1). In addition, in presence of light, the ferrioxalate would be converted to insoluble ferrous oxalate(2).

At/

(1) Abegg, 'Handb. d. anorg. Chem., Bd. IV, 3A btlg, 2 Tl, B 482, 558.

Friend, Text of inorg. Chem., Vol. IX, Pt.2, p.207.

(2) Abegg, op. cit. p. 150.

At the commencement of the work it was hoped to determine (1) the extent to which oxalate ion was adsorbed by the colloidal particles and (2) the extent to which acid was liberated from the particles by the action of salts, by means of quantitative analysis of the ultrafiltrate. Owing, however, to the complexity of the ultrafiltrate, the numerous attempts made to estimate the appropriate constituents proved unsuccessful.

TABLE IV.

Analysis of Coagulum Sol A.

Normality of HCl = 0.01052 N.

Normality of NaOH = 0.009305 N.

(19.99 mls HCl = 22.60 mls NaOH)

Salt	Salt Conc.	Volume of NaOH used in Back titration (mls.)	Mean Volume	Milliequivalents of alkali from 25 mls. sol.
0	0	22.61 22.64	22.62	- 0.0002
K_2SO_4	1 N	0.53 0.57	0.55	+ 0.2052
Na_2SO_4	1 N	3.01 2.92 2.97	2.97	+ 0.1827
$MgSO_4$	1 N	13.02 12.97 13.45	13.15	+ 0.0879
Li_2SO_4(1)	0.5 N	23.20 23.12	23.16	-
Li_2SO_4(2)	0.5 N	22.36 22.32	22.34	+ 0.0024
Li_2SO_4(3)	0.5 N	22.35 22.07	22.21	+ 0.0036

Fig. 5.

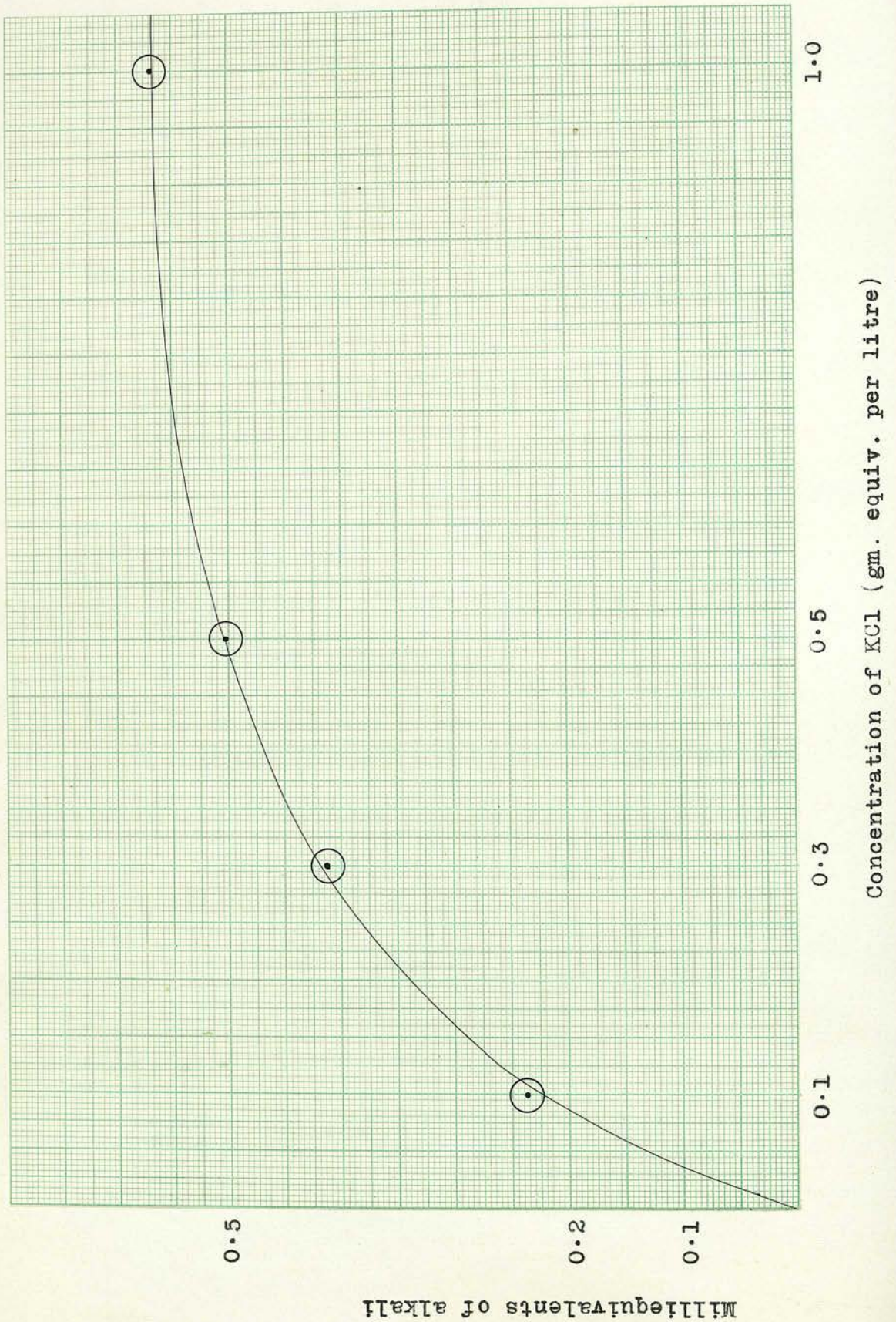

Milliequivalents of alkali
0·5
0·2
0·1
0·1
0·3
0·5
1·0
Concentration of KCl (gm. equiv. per litre)

TABLE V.

Sol B - Analysis of Coagulum.

Normality of HCl = 0.01052

Normality of NaOH = 0.00939

Salt Concentration	Volume of HCl	Volume of NaOH used in back titration	Mean Volume	Milliequivalents of alkali from 25 mls sol.
1.0 KCl	60	6.47		
		6.65	6.56	0.5696
0.5 "	50	2.78		
		2.27	2.53	0.5023
0.3 "	50	11.91		
		12.35	12.13	0.4121
0.1 "	50	30.88		
		30.46	30.67	0.2381

DETERMINATION OF LIBERATED ACID.

The amounts of acid liberated from the colloidal micelles by the action of salts were determined in the following manner. Two mls. of a salt solution of known concentration were added to two mls. of sol in a pyrex glass test-tube fitted with a ground-in stopper. The contents of the tube were thoroughly mixed by shaking, allowed to stand for one hour at room temperature, and then centrifuged at 9500 revs. per minute (7200 g) for 15 minutes. If coagulation was complete, two mls. of the supernatant liquid were pipetted into a Jena glass bottle and the volume made up to 8 mls. by the addition of 2 x 3 mls.[1] of a solution of the same salt of such a concentration that the final concentration of salt was brought to a pre-arranged value[2]. The value of Δ E (see p. 24) for this test solution was then determined.

If coagulation did not occur or was incomplete, the mixture of sol + salt was ultrafiltered by means of the low pressure apparatus (see p.15) and 2 mls. of the ultrafiltrate made up to 8 mls. with salt solution as described above.

The/

(1) See p.12 for calibration of pipettes.

(2) For example in the case of potassium chloride, 2 mls. supernatant liquid (or ultrafiltrate) were added to 2 x 3 mls x M KCl , where x was chosen so that the final concentration of salt was 1 M in every case.

The amount of acid present in the intermicellar liquid of the sol before the addition of a salt was found by ultrafiltering 2 mls sol + 2 mls water, and determining Δ E for the 'test' solution:- 2 mls ultrafiltrate + 2 mls water + 2 x 2 mls 2 M KCl.

In order to deduce the actual concentration of acid in the 'test' solution from the e.m.f. measurements it was necessary to obtain the values of ΔE given by known concentrations of acid in the presence of the particular concentration of salt in question. A stock solution of hydrochloric acid was prepared from A.R. acid, its concentration determined by titration with carbonate-free sodium hydroxide, and suitable concentrations of acid obtained by dilution. Mixtures were then made of equal volumes of acid and salt solution, so that the final concentration of the salt was that selected for the 'test' solution (e.g. 1 M in the case of KCl ; see footnote on p. 39). The Δ E values for these acid-salt mixtures are reproduced in Tables VI to XI and figs.6 to 11 . The concentration of acid corresponding to any given value of ΔE was obtained from the appropriate graph by interpolation.

The pH values of the salt solutions themselves were determined by means of the glass electrode and are listed in Table XII . It will be seen that these solutions contained only negligible quantities of acid or alkali.

The/

The method of calculating the amounts of liberated acid is given on page 55 , and the data obtained in Tables

TEST OF POTASSIUM FERRIOXALATE AS PEPTISING AGENT.

Small portions of solid prussian blue (prepared as described on page 28) were thoroughly washed with distilled water and then vigorously shaken with solutions of potassium ferrioxalate (prepared from a pure sample supplied by B.D.H.) at various concentrations. The prussian blue showed no tendency to disperse to form a sol at any concentration of the ferrioxalate. Peptisation immediately occurred, however, when a small quantity of oxalic acid was added to a coarse suspension of the blue in potassium ferrioxalate solution.

Fig. 6.

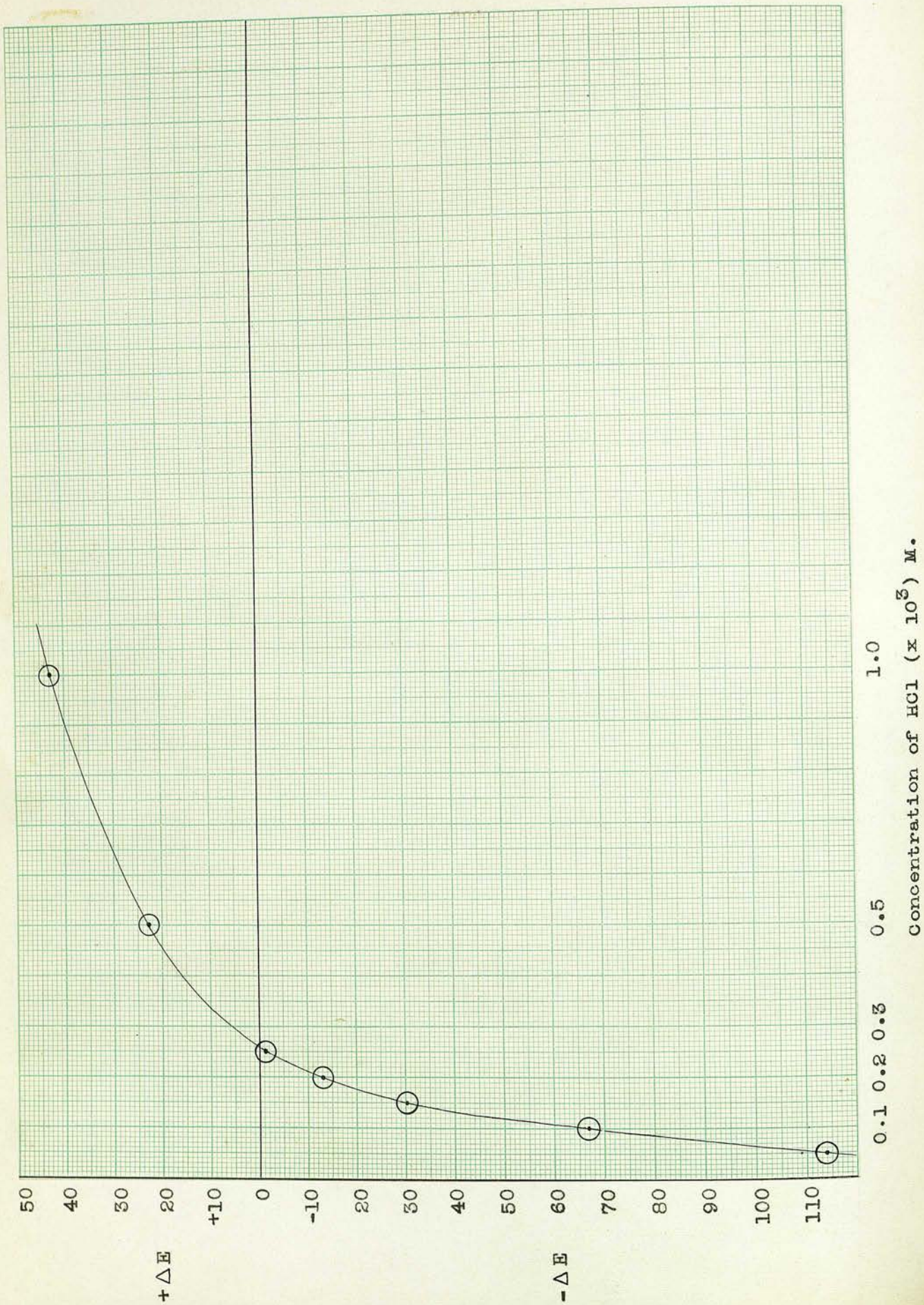

50
40
30
20
+10
0
-10
20
30
40
50
60
70
80
90
100
110
+ ΔE
- ΔE
0.1 0.2 0.3 0.5 1.0
Concentration of HCl (x 10^{3}) M.

TABLE VI.

Values of ΔE for LiCl - HCl mixtures.

Concentration of salt.	Concentration of acid.	ΔE.	Mean ΔE.
0.5	1000	+ 42.5	
		+ 43.6	+ 43.0
	500	+ 22.8	
		+ 22.5	+ 22.7
	250	- 1.7	
		- 0.7	
		- 0.8	- 1.1
	200	- 14.1	
		- 11.9	- 13.0
	150	- 30.7	
		- 29.7	- 30.2
	100	- 68.2	
		- 65.6	- 66.9
	50	-112.6	
		-115.3	-113.9

Note. In all tables salt concentrations are expressed in grm. equivalents per litre, acid concentrations in micro mols per litre, and values of ΔE in millivolts.

Fig. 7.

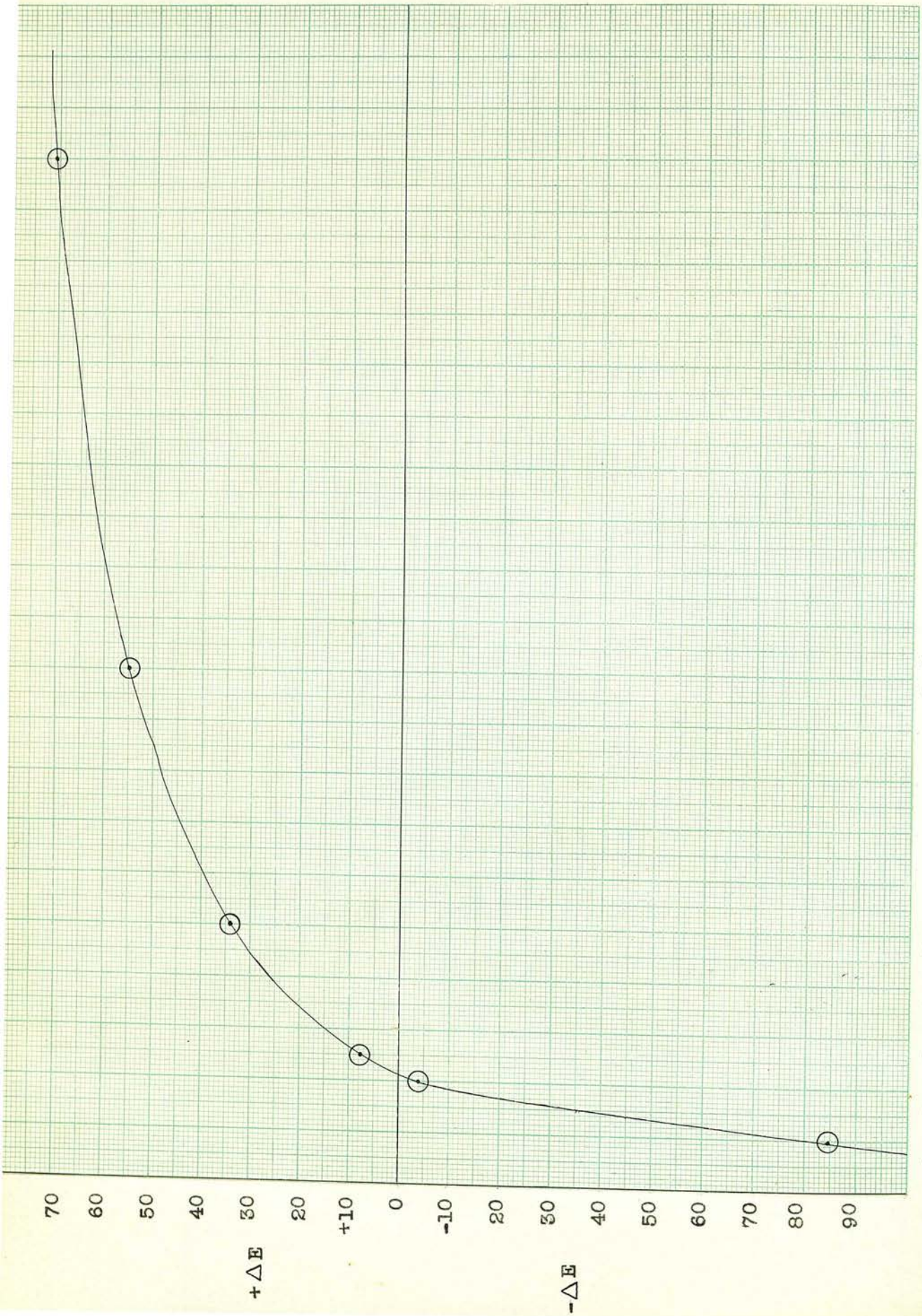

+ΔE
70
60
50
40
30
20
+10
0
-10
20
30
40
50
60
70
80
90
-ΔE
0.1 0.2 0.3 0.4 0.5
1.0
2.0
Concentration of HCl (x 10³) M.

TABLE VII.

Values of $\triangle E$ for NaCl - HCl mixtures.

Concentration of salt.	Concentration of acid.	$\triangle$ E.	Mean $\triangle$ E.
1.0 N	2000	+ 70.9	
		+ 70.2	+ 70.6
	1000	+ 55.2	
		+ 54.3	+ 54.8
	500	+ 34.0	
		+ 34.1	+ 34.0
	250	+ 7.6	
		+ 8.1	+ 7.9
	200	- 4.4	
		- 3.5	- 4.0
	100	- 84.8	
		- 82.5	- 83.7
	50	- 131.3	
		- 129.8	- 130.1

Fig. 8.

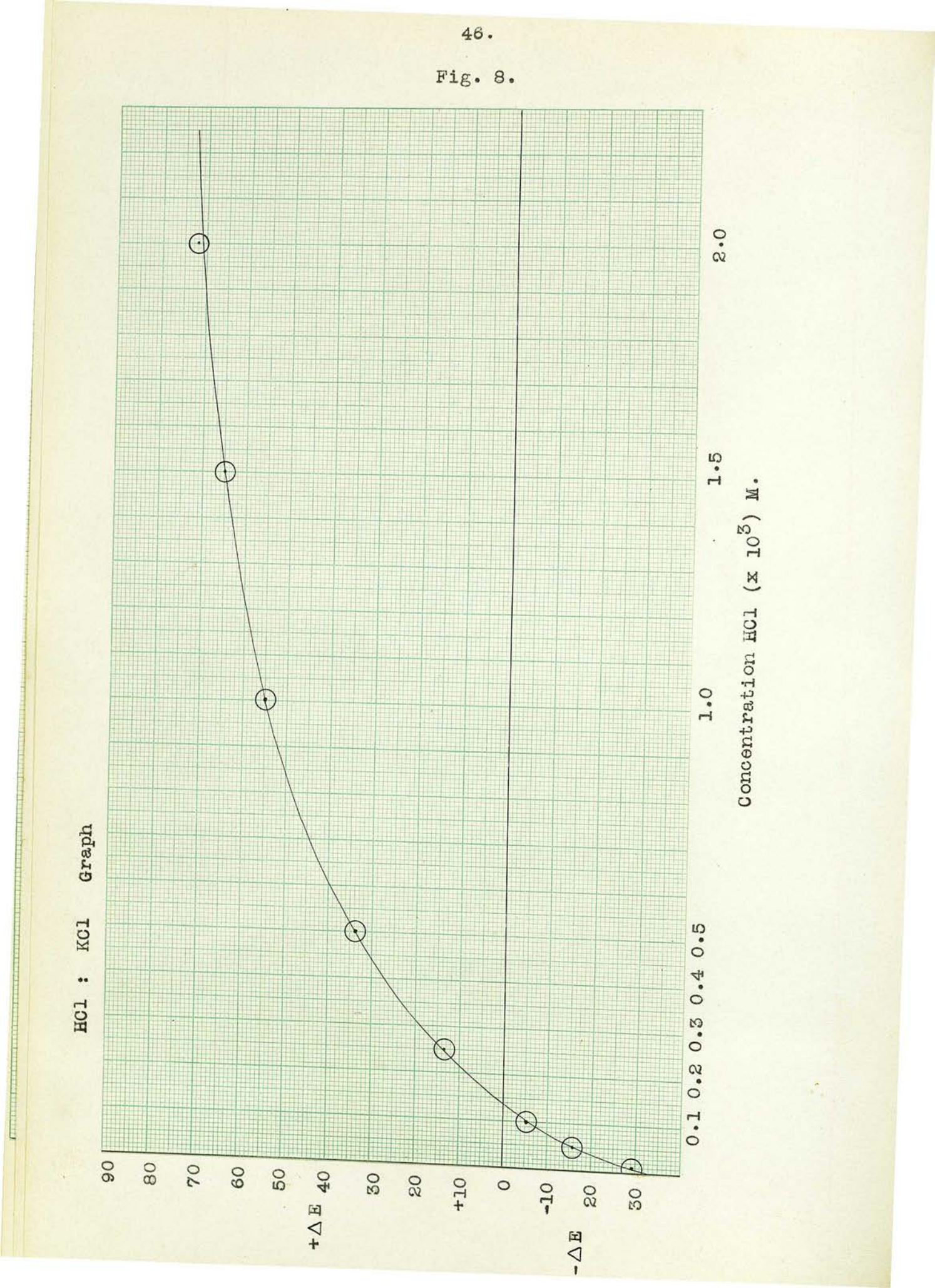

HCl : KCl Graph
90
80
70
60
50
+ΔE 40
30
20
+10
0
-10
20
30
-ΔE
0.1 0.2 0.3 0.4 0.5
1.0
1.5
2.0
Concentration HCl (x 10³) M.

TABLE VIII.

Values of ΔE for KCl - HCl mixtures.

Concentration of salt.	Concentration of HCl.	ΔE.	Mean ΔE.
1.0 N	2000	+ 71.7	
		+ 72.3	+ 72.0
	1500	+ 65.4	
		+ 64.5	+ 64.9
	1000	+ 55.4	
		+ 54.4	+ 54.9
	500	+ 33.6	
		+ 34.0	+ 33.8
	250	+ 12.9	
		+ 11.8	
		+ 15.6	+ 13.4
	100	- 5.8	
		- 4.5	- 5.2
	50	- 16.4	
		- 15.2	- 15.8
	10	- 29.8	
		- 28.3	- 29.1

HCl : CSCl Graph Final Salt Concentration 0.5 M.

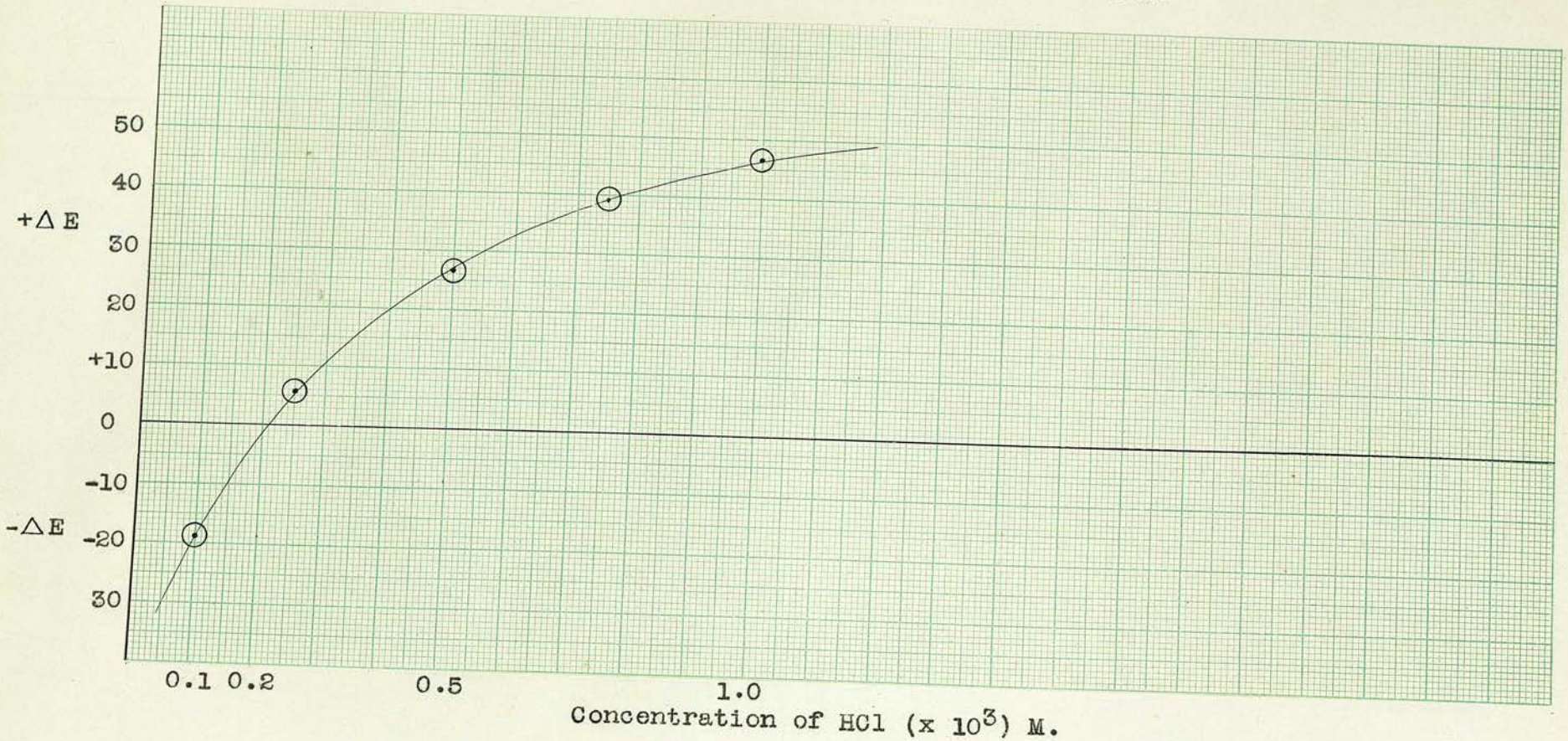


Fig. 9.

TABLE IX.

Values of $\triangle E$ for CS Cl - HCl mixtures.

Concentration of salt.	Concentration of acid.	$\triangle E$.	Mean $\triangle E$.
0.5	1000	+ 46.9	
		+ 46.1	+ 46.5
	750	+ 39.2	
		+ 39.0	+ 39.1
	500	+ 27.6	
		+ 25.6	
		+ 26.5	+ 26.6
	250	+ 6.0	
		+ 5.6	
		+ 5.7	
		+ 6.2	+ 5.9
	100	- 19.3	
		- 18.2	- 18.8

Fig. 10.

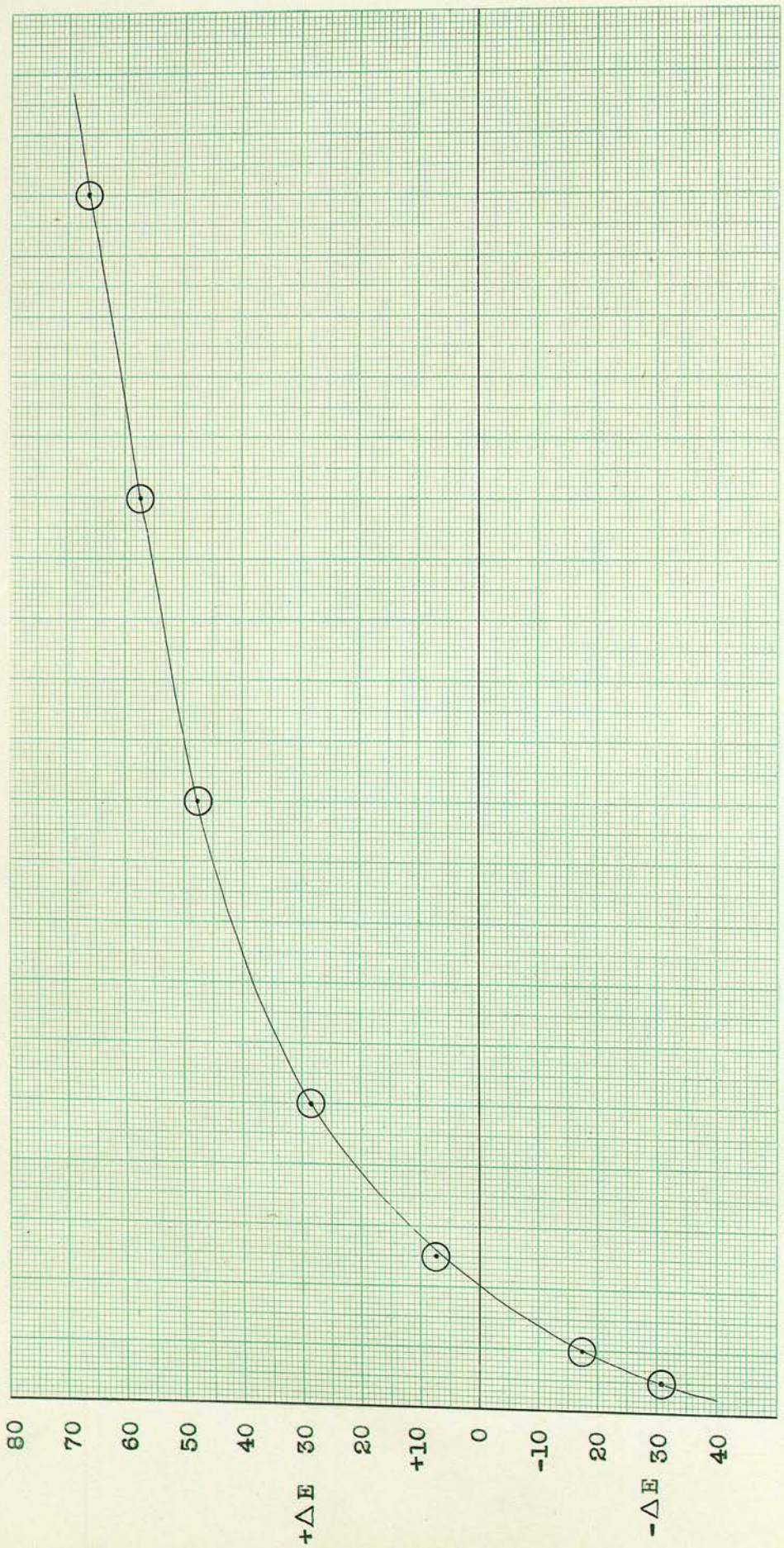

HCl: $MgCl_2$ Graph
80
70
60
50
40
30
20
+10
0
-10
20
30
40
+ΔE
-ΔE
0.1 0.2 0.3 0.5 1.0 1.5 2.0
Concentration of HCl (x 10^{-5}) M.

TABLE X.

Values of ΔE for $MgCl_2$ - HCl mixtures.

Concentration of salt.	Concentration of acid.	ΔE.	Mean ΔE.
0.5	2000	+ 66.6	
		+ 65.9	+ 66.3
	1500	+ 57.3	
		+ 56.9	+ 57.1
	1000	+ 47.9	
		+ 47.0	+ 47.5
	500	+ 28.5	
		+ 28.0	+ 28.3
	250	+ 7.6	
		+ 6.5	+ 7.1
	100	- 18.0	
		- 16.7	- 17.4
	50	- 30.8	
		- 30.9	- 30.9

HCl: $PbCl_2$ Graph

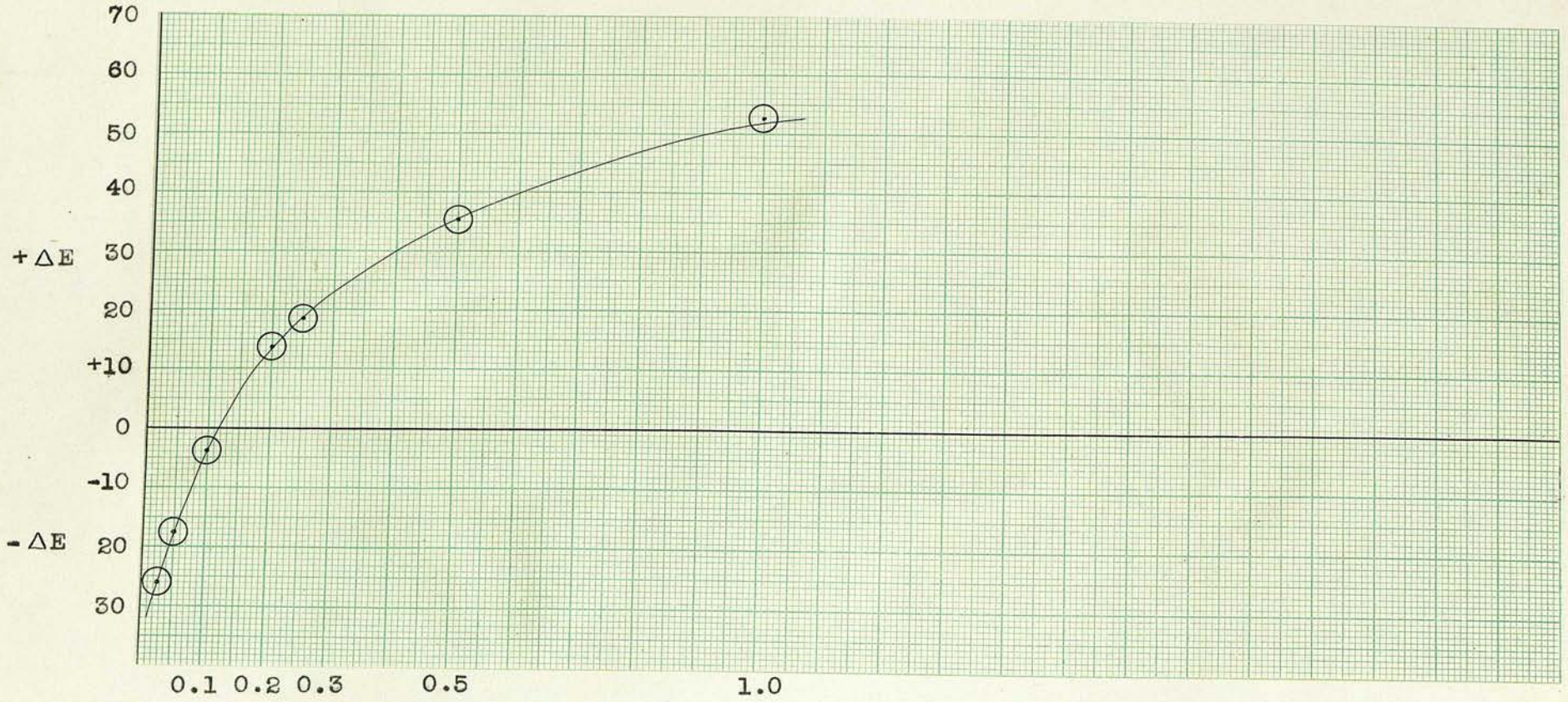


Fig. 11.

TABLE XI.

Values of ΔE for $PbCl_2$ - HCl mixtures.

Concentration of salt.	Concentration of acid.	ΔE.	Mean ΔE.
0.02	1000	+ 52.4	
		+ 53.4	+ 52.9
	500	+ 35.1	
		+ 35.1	
		+ 35.2	+ 35.1
	250	+ 18.6	
		+ 18.1	+ 18.4
	200	+ 14.1	
		+ 13.7	
		+ 14.0	+ 13.9
	100	- 4.3	
		- 3.5	- 3.9
	50	- 17.3	
		- 17.6	- 17.5
	25	- 25.1	
		- 26.8	- 26.0

TABLE XII.

pH Values for Salt Solutions.

Salt	Salt Concentration	pH
LiCl	1.0	8.05
LiCl	0.2	7.57
NaCl	2.0	7.52
NaCl	0.2	7.04
KCl	2.0	6.23
KCl	0.2	6.62
CsCl	1.0	8.13
$PbCl_2$	0.2	5.51
$MgCl_2$	1.0	6.60
$MgCl_2$	0.2	6.66

CALCULATION OF LIBERATED ACID.

The following example illustrates the method of calculating the concentration of liberated acid.

Concentration of acid liberated by 0.3 M KCl in the case of sol C (Table XIV).

Initial mixture = 2 mls sol C + 2 mls 0.6 M KCl , i.e. concentration of salt in mixture = 0.3 M. At this concentration coagulation was complete.

'Test' solution = 2 mls supernatant liquid from initial mixture + 6 mls 1.233 M KCl, i.e. concentration of salt in solution = 1 M .

Mean value of ΔE for 'test' solution = + 32.8 m.v. (Table XIV). Hence concentration of acid in 'test' solution = 485 micromols per litre (by interpolation on graph in Fig. 8).

Thus concentration of acid in initial mixture (called 'Total Acid' for convenience) = $\frac{6 + 2}{2}$ x 485 = 1940 micromols per litre.

Two mls sol C + 2 mls H_2O ultrafiltered, and a 'test' solution prepared as follows:- 2 mls ultrafiltrate + 2 mls H_2O + 4 mls 2 M KCl.

Mean value ΔE for this solution = - 16.5 (Table XIII). Hence concentration of acid in 'test' solution = 47.5 micromols per litre (from graph p.46 in Fig. 8).

Thus concentration in mixture:- 2 mls sol + 2 mls water = $\frac{2 + 2 + 4}{2}$ x 47.5 = 190 micromols per litre.

Hence concentration, in initial sol + salt mixture, of acid liberated by the salt (called 'Liberated Acid for convenience) = 1940 - 190 = 1750 micromols per litre.

TABLE XIII.

Concentration of Intermicellar Acid in the System:-

Sol + Equal Volume Water.

Sol	Date	△E	Mean △E	Concentration of acid.
C	-	- 17.0		
		- 16.0	- 16.5	190
D	26:5:36	- 14.3		
		- 14.5	- 14.4	220
"	18:6:36*	- 109.3		
		- 107.6	- 108.5	210
E	14:10:36	- 30.5		
		- 34.7	- 32.6	14
"	27:1:37	- 3.7		
		- 1.7	- 2.7	240
"	25:2:37x	+ 0.8		
		+ 2.8	+ 1.8	256
F	9:3:37	+ 6.8		
		+ 6.3	+ 6.6	368

* In this case, the 'test' solution was:- 2 mls. ultrafiltrate + 2 mls water + 4 mls 1.0 M LiCl.

x In this case, the 'test' solution was:- 2 mls ultrafiltrate + 2 mls water + 4 mls 0.04 M $PbCl_2$.

TABLE XIV.

Liberation of Acid (Sol C)

Salt and Concentration.	ΔE	Mean ΔE	Total Acid.	Liberated Acid.
KCl				
1.0	+ 34.5			
	+ 34.6	+ 34.5	2050	1860
0.3	+ 33.1			
	+ 32.5	+ 32.8	1940	1750
0.1	+ 30.3	+ 30.3	1800	1610
0.05	+ 31.0	+ 31.0	1840	1650
0.025	+ 30.6			
	+ 28.7	+ 29.7	1750	1560
0.01	+ 24.6			
	+ 23.8	+ 24.2	1460	1270
0.005	+ 17.7	+ 17.7	1150	960
LiCl				
0.5	+ 41			
	+ 3.1	+ 3.6	1140	950
0.1	+ 3.7			
	+ 3.1	+ 3.4	1140	950
0.05	- 0.2	- 0.2	1030	840
0.025	- 3.0	- 3.0	976	786

TABLE XV.

Liberation of Acid (Sol D).

Salt and Concentration.	△E	Mean △E	Total Acid	Liberated Acid
KCl				
1.0	+ 34.4			
	+ 33.5	+ 33.9	2000	1785
0.5	+ 32.9			
	+ 32.4	+ 32.7	1950	1735
0.1	+ 31.9			
	+ 32.7	+ 32.3	1940	1725
0.05	+ 31.1			
	+ 30.3	+ 30.7	1840	1625
0.025	+ 30.0			
	+ 29.8	+ 29.9	1800	1585
0.01	+ 25.9			
	+ 24.9	+ 25.4	1580	1365
0.005	+ 14.9			
	+ 14.0	+ 14.5	1080	865
NaCl				
1.0	+ 30.0			
	+ 29.5	+ 29.7	1770	1555
0.1	+ 27.4			
	+ 26.5	+ 27.0	1640	1425
0.025	+ 21.2			
	+ 20.9	+ 21.0	1400	1185
0.005	- 44.0	- 44.0	575	360

TABLE XVI.

Liberation of Acid (Sol D).

Salt and Concentration.	ΔE	Mean ΔE	Total Acid	Liberated Acid.
$MgCl_2$				
0.5	+ 26.1			
	+ 26.1	+ 26.1	1880	1665
0.1	+ 23.2			
	+ 23.0	+ 23.1	1710	1495
0.025	+ 19.4			
	+ 18.7	+ 19.0	1520	1305
0.005	+ 15.8	+ 15.8	1370	1155
LiCl				
0.5	+ 6.3			
	+ 6.1	+ 6.2	1230	1015
0.1	+ 5.6			
	+ 4.4	+ 5.0	1190	975
0.05	+ 3.6			
	+ 3.1	+ 3.3	1130	915
0.025	+ 1.1			
	- 0.5	- 0.8	1020	805
0.01	- 56.2			
	- 57.7	- 56.9	440	225

TABLE XVII.

Liberation of Acid (Sol E).

Salt and Concentration.	Δ E	Mean Δ E	Total Acid	Liberated Acid
KCl				
1.0	+ 32.1			
	+ 31.5	+ 31.8	1890	1876
0.3	+ 33.1			
	+ 32.7	+ 32.9	1940	1926
0.1	+ 29.8			
	+ 28.7			
	+ 28.8			
	+ 29.6	+ 29.2	1760	1746
0.003	+ 11.1			
	+ 10.7	+ 10.9	880	866
LiCl				
0.5	- 4.1			
	- 4.5	- 4.3	948	934
0.3	- 6.9			
	- 6.5	- 6.7	904	890
0.1	- 11.1			
	- 11.6	- 11.4	828	814
0.011	- 30.1			
	- 29.4	- 29.8	600	586

TABLE XVIII.

Liberation of Acid (Sol E)

Salt and Concentration.	△ E	Mean △E	Total Acid	Liberated Acid
NaCl				
1.0	+ 22.0			
	+ 23.8	+ 22.9	1470	1456
0.3	+ 23.5			
	+ 22.9	+ 23.2	1480	1466
0.1	+ 20.2			
	+ 21.3	+ 20.8	1390	1376
0.05	+ 16.5			
	+ 17.5	+ 17.0	1270	1256
0.025	+ 12.7			
	+ 12.5	+ 12.6	1130	1116
0.01	+ 4.8			
	+ 5.0	+ 4.9	944	930
0.0048	- 9.8			
	- 8.5	- 9.2	752	738
$MgCl_2$				
0.5	+ 16.0			
	+ 16.4	+ 16.2	1390	1376
0.1	+ 14.7			
	+ 13.6	+ 14.2	1310	1296
0.025	+ 10.8			
	+ 9.9	+ 10.4	1140	1126
0.005	+ 5.0			
	+ 5.0	+ 5.0	968	954

TABLE XIX.

Liberation of Acid (Sol E).

Salt and Concentration.	Δ E	Mean Δ E	Total Acid.	Liberated Acid.
CsCl				
0.5	+ 32.2			
	+ 33.0	+ 32.6	2390	2376
0.5	+ 41.1	+ 41.1	3240	3226
0.3	+ 36.0	+ 36.0	2690	2676
0.5	+ 33.9	+ 33.9	2510	2496
0.3	+ 34	+ 34.0	2510	2496

TABLE XX.

Liberation of Acid (Sol E).

Salt and Concentration.	Δ E	Mean Δ E	Total Acid	Liberated Acid.
$PbCl_2$				
0.02	+ 27.0			
	+ 25.3	+ 26.2	1360	1120
0.01	+ 26.1			
	+ 26.1	+ 26.1	1360	1120
0.02	+ 26.3	+ 26.3	1360	1120
0.0025	+ 23.5	+ 23.5	1220	980
0.001	+ 12.5			
	+ 13.2	+ 12.9	792	552
0.00095	+ 9.8			
	+ 9.8	+ 9.8	688	448

TABLE XXI.

Values of Maximum Total Acid (Sol E).

Date	Salt and Concentration.	ΔE	Mean ΔE	Total Acid	Mean Total Acid
	KCl				
15:10:36	1.0	+ 32.1			
		+ 31.5	+ 31.8	1890	
22:2:37	1.0	+ 33.1			
		+ 32.0	+ 32.6	1920	1905
	NaCl				
20:10:36	1.0	+ 22.0			
		+ 23.8	+ 22.9	1470	
20:2:37	1.0	+ 23.2	+ 23.2	1480	1475
	$MgCl_2$				
20:10:36	0.5	+ 16.0			
		+ 16.4	+ 16.2	1390	
16:2:37	0.5	+ 14.8			
		+ 14.0	+ 14.4	1316	1353
	LiCl				
15:10:36	0.5	- 4.1			
		- 4.5	- 4.3	948	
12:2:37	0.5	- 5.7			
		- 4.3	- 5.0	940	944

TABLE XXII.

Liberation of Acid at the Coagulation Point (Sol E).

Date	Salt and Concentration.	Δ E	Mean Δ E	Total Acid	Liberated Acid.
	KCl				
17:12:36	0.003	+ 11.1			
		+ 10.7	+ 10.9	880	
23:2:37	"	+ 9.5			
		+ 9.7	+ 9.6	832	
				Mean:856	616
	NaCl				
17:12:36	0.0048	- 9.8			
		- 8.5	- 9.2	752	
24:2:37	0.0048	- 8.1			
		- 9.0	- 8.6	748	
				Mean:750	510
	LiCl				
17:12:36	0.011	- 30.1			
		- 29.4	- 29.8	600	
9.2.37	0.011	- 31.9			
		- 30.3	- 31.1	596	
				Mean:598	358
	$MgCl_2$				
16:2:37	0.00186	+ 2.1			
		+ 0.2	+ 1.2	864	
23:2:37	0.00186	+ 1.4			
		+ 1.4	+ 1.4	864	
				Mean:864	624
	$PbCl_2$				
9:2:37	0.00095	+ 9.8			
		+ 9.8	+ 9.8	688	448

TABLE XXIII.

Liberation of Acid (Sol F)

Salt and Concentration.	△ E	Mean △E	Total Acid	Liberated Acid
KCl				
1.0	+ 38.1			
	+ 38.5	+38.3	2300	1932
NaCl				
1.0	+ 30.9			
	+ 31.2	+ 31.1	1840	1472
LiCl				
0.5	+ 9.1			
	+ 9.1	+ 9.1	1324	956
$MgCl_2$				
0.5	+ 23.1			
	+ 22.6	+ 22.9	1700	1332

DETERMINATION OF COAGULATION VALUES.

At salt concentrations just below those required for complete coagulation, the greater part of the prussian blue settled out, (very slowly unless the liquid was centrifuged) leaving a pale blue supernatant liquid. The assumption was made that the same stage in the coagulation process was reached for the different salts when the intensity of the colour in the supernatant liquid was the same. Hence the following procedure was adopted for determining the 'coagulation values' of the salts.

Two mls of sol were added to two mls of the salt solution in a pyrex tube fitted with a ground-in glass stopper. In order to minimise local variations in concentration during mixing, the liquids were discharged simultaneously from pipettes at approximately the same rate and in such a manner that the streams of liquid intermingled. The mixture was shaken vigorously for two minutes and allowed to stand at room temperature for 15 minutes. It was then transferred to a small centrifuge tube and centrifuged for 15 minutes at 9500 revs. per minute. Two mls. of the supernatant liquid were withdrawn from the centrifuged mixture of sol and electrolyte and the volume made up to ten mls. The intensity of the blue coloration in this/

this solution was measured by means of the photometer, described on p. 26 . The coagulation value of any salt was taken as the concentration at which the amount of prussian blue remaining in the supernatant liquid gave a photometer reading of 80 (i.e. x - 50 = 30).

The results are shown in Tables XXIV to XXVII.

TABLE XXIV.

Coagulation Values (Sol E).

Salt and Concentration.	Photometer Reading (x)	x - 50		Coagulation Value
LiCl				
0.011	80.2	30.2		
"	71.5	21.5		
"	90.7	40.7		
"	89.5	39.5		
"	82.0	32.0	31.2	0.011
"	78.5	28.5		
"	78.5	28.5		
"	79.0	29.0		
NaCl				
0.008	50.8	0.8		
0.006	58.9	8.9		
0.005	64.2	14.2		
0.0047	78.3	28.3		
"	77.8	27.8	28.4	0.0047
"	79.0	29.0		
0.0040	91.0	41.0		

TABLE XXV.

Coagulation Values (Sol E).

Salt and Concentration.	Photometer Reading (x)	x - 50		Coagulation Value
KCl				
0.005	50.5	0.5		
0.0035	72.5	22.5		
0.003	90.8	40.8		
"	83.5	33.5	31.9	0.0030
"	81.0	31.0		
"	81.5	31.5		
0.002	99.5	49.5		
$MgCl_2$				
0.003	51	1.0		
0.002	65.5	15.5		
0.00186	80.5	30.5		
"	82.0	32.0	31.3	0.00186
"	81.5	31.5		
0.0016	94.5	44.5		

TABLE XXVI.

Coagulation Values (Sol E).

Salt and Concentration.	Photometer Reading (x)	x - 50		Coagulation Value
$PbCl_2$				
0.001	68.5	18.5		
"	68.0	18.0		
"	69.5	19.5		
0.00095	80.5	30.5		
"	76.5	26.5		
"	79.0	29.0		
"	77.0	27.0	26.1	0.00095
"	73.0	23.0		
"	70.5	20.5		
0.00090	90.5	40.5		

TABLE XXVII.

Coagulation Values (Sol F).

Salt and Concentration.	Photometer Reading (x)	x - 50		Coagulation Value.
LiCl				
0.0196	80.3	30.3		
"	82.5	32.5	31.6	0.0196
"	82.0	32.0		
0.0188		47.5		
KCl				
0.0056	69.5	19.5		
0.0051	79.5	29.5		
"	81.5	31.5	30.1	0.0051
"	79.3	29.3		

D I S C U S S I O N.

Constitution of Sols.

The prussian blue was in every case prepared by the addition of 2 gms of potassium ferrocyanide in 100 mls water to 2 gms ferric chloride in 100 mls water. Thus the molar ratio of the reactants was uniformly 1 mol. ferric salt to 0.44 mol. ferrocyanide. According to the data of Müller, Hofmann and others[1], the blue obtained under these conditions is free from potassium and has the composition $Fe^{III}_4\left[Fe^{II}(CN)_6\right]_3$. This result is supported by the present work since, as will be seen from Table IV (p. 36), analysis of the disperse phase in the undialysed sols showed that (in the absence of added salt) the colloidal particles or micelles contained no alkali metal.

The action of oxalic acid upon this so-called 'insoluble' blue does not appear to have been closely investigated. Justin-Mueller[2] suggests that (1) only one/

(1) Müller, J. prakt. Chem., 84, 353, (1911).
Hofmann, Heine and Hochtlein, Liebig's Ann., 337, 1, (1904).
Friend, "Textbook of Inorganic Chem.", Vol. IX, Pt. II, 226-227, (1921).
Abegg, "Handb. d. anorg. Chem., Bd. IV, 3A btlg, 2Tl, B 559-574, (1930)_

(2) Justin-Mueller, Bull. Soc. Chem., 49, 1285, (1931).

one of the ferric atoms is attacked by the oxalic acid, the reaction being as follows:

$$2Fe_4^{iii}\left[Fe^{ii}(CN)_6\right]_3 + 3H_2C_2O_4 \longrightarrow 6HFe^{iii}Fe^{ii}(CN)_6 + Fe_2(C_2O_4)_3$$

and (2) that 'peptisation' of the insoluble blue is due to its conversion into the compound $HFe^{iii}Fe^{ii}(CN)_6$, which is regarded as analogous to the 'soluble' blue of composition $KFe^{iii}Fe^{ii}(CN)_6$.(1) Qualitative analysis of the ultrafiltrates from undialysed sols (see p.p.32 33) revealed, however, that the intermicellar liquid in these systems contained considerable amounts of ferrocyanide ion, together with ferrioxalate ion. Thus the oxalic acid had completely decomposed a portion of the 'insoluble' blue according to the equation:

$$Fe_4^{iii}\left[Fe^{ii}(CN)_6\right]_3 + 12H_2C_2O_4 \rightleftharpoons 3H_4Fe(CN)_6 + 4H_3Fe(C_2O_4)_3$$

There was evidence that the action of the oxalic acid rapidly reached a condition of equilibrium. The colour of the ultrafiltrate obtained twenty minutes after peptisation was just as intense as when the sol was ultrafiltered fourteen days, or even three months after preparation, provided the same amount of blue was present. As the quantity of blue was increased the colour/

(1) Friend, loc. cit. 225-226; Abegg, loc. cit. 559-574.

colour of the filtrate also deepened. Moreover the fact that the ultrafiltrate turned blue when a little potassium ferrocyanide was added (see p. 33) also indicates that the reaction between prussian blue and oxalic acid is reversible. Kohn[1] reports that both 'insoluble' and 'soluble' blue are completely soluble in solutions of potassium oxalate and potassium hydrogen oxalate, even at ordinary temperatures, but the concentrations of these substances employed in his experiments were much higher than that of the oxalic acid used in the present work.

Direct experiment (see p. 41) showed that the actual peptisation of the prussian blue is not due to adsorption of the ferrioxalate ions formed in the reaction between the blue and the oxalic acid. It is also improbable that peptisation is due to adsorption of simple oxalate ions, as postulated by Weir[2], since cupric ferrocyanide which is chemically very similar to prussian blue, is not peptised by oxalic acid or potassium oxalate.[3] On the other hand it appears certain that peptisation will occur through the adsorption of ferrocyanide ions by the particles composing/

(1) Kohn, Monats. f. Chem., 66, 393, (1935).

(2) Weir, J.C.S., 127 2245, (1925).

(3) Graham, Lieb. Ann., 121, 48, (1862).

composing the precipitate of prussian blue. In the present research it was found that the blue was peptised by hydroferrocyanic acid, and it is well known that prussian blue and cupric ferrocyanide are peptised by potassium ferrocyanide(1). Weiser and Milligan(2) have also prepared sols of cupric ferrocyanide by peptisation with hydroferrocyanic acid. Moreover ferrocyanide ion has a strong stabilising influence on sols in general(3), which oxalate ion does not possess. Thus for example, Hazel and Ayres(4) succeeded in converting positive sols of ferric oxide into stable negative systems by the addition of potassium ferrocyanide. In the present research (see p. 7o) it was found that the addition of hydroferrocyanic acid to a sol increased the concentration of salt necessary to produce coagulation.

As the result of dialysis, the concentration of acid in the intermicellar liquid decreased from about 0.3N to concentrations of the order 0.0025N (see Table/

(1) Abegg, loc. cit., 626, 630; Bachmann, Zeit, anorg, Chem., 100, 90, 1917).

(2) Weiser and Milligan, J. Phys. Chem., 40, 1071, (1936).

(3) Abegg, loc. cit., 636.
Weiser, Chapter XVIII in "The Colloidal Salts" (New York), 1928.
Weiser, J. Phys. Chem., 30, 1527, (1926).

(4) Hazel and Ayres, J. Phys. Chem., 35, 3148, (1931).

Table XIII). It seems probable that some desorption of hydroferrocyanic acid will occur during dialysis, and also that the prussian blue will be hydrolysed to a small extent, thus:

$$Fe_4^{iii}\left[Fe^{ii}(CN)_6\right]_3 + 12H_2O \longrightarrow 3H_4Fe(CN)_6 + 4Fe(OH)_3$$

Hazel and Sorum[(1)] found that hydrolysis occurred rapidly when prussian blue sol was dropped into boiling water, and during the present work it was frequently observed that hydrolysis took place relatively quickly when a dialysed sol was exposed to bright sunlight[(2)]. It is therefore reasonable to suppose that hydrolysis tends to occur even in the dark and at ordinary temperatures. This would account for an observation made during the preparation of the sols. On one occasion a precipitate of 'insoluble' blue, protected from the action of light, was washed with water for a period much longer than the normal (see p. 28) and was then found to peptise spontaneously. Apparently hydrolysis had occurred to the extent of yielding enough hydroferrocyanic acid to peptise the precipitate.

It will be seen from Table (p. 56) that the concentration/

(1) Hazel and Sorum, J. Am. C.S., 52, 1337, (1930).

(2) See also Bachmann, loc. cit. 89.

concentration of acid in the intermicellar liquid of Sol E immediately after dialysis was 14 micro-equivalents per litre (m.e./l.) At the end of about three months the acidity had risen to 240 m.e./l., at which value it remained practically constant for the remainder of the experimental period. The increase seems to have been due to desorption of hydroferrocyanic acid, since the 'total' acid (i.e. original intermicellar acid + liberated acid) did not alter (Table XXI p. 63).

Sol F was prepared by adding solid hydroferrocyanic acid to a portion of Sol E. Hence the concentration of prussian blue was the same in the two sols. If none of the added acid had been taken up by the colloidal particles, the concentration of acid in the intermicellar liquid of a mixture of equal vols. of Sol F and water would have exceeded that in a similar mixture of Sol E and water, by 968 m.e./l. ($\frac{1935}{2}$: see p. 30). Actually it was found that the increase was 128 m.e./l. (368 - 240; Table XIII). Thus 840 m.e./l. were adsorbed by or had combined with, the particles. The maximum liberation of hydrogen, however, was increased by only 244 m.e./l. (Table XXVIII) beyond that in the case of Sol E. Thus about 71 per cent of the added acid combined with the prussian blue so that the hydrogen became irreplaceable. The simplest explanation/

SOL C.

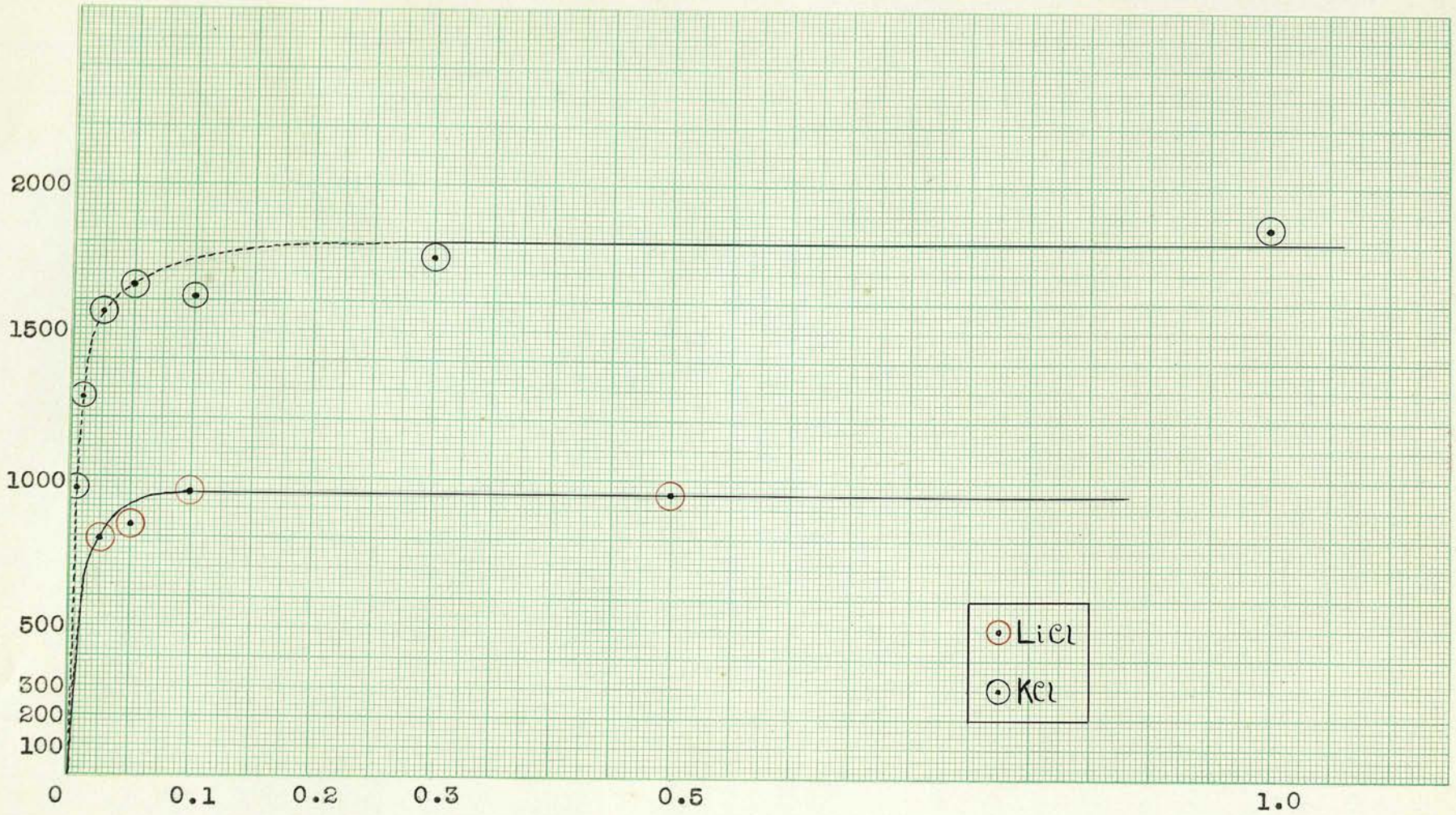

Micromols. Liberated Hydrogen ion.
2000
1500
1000
500
300
200
100
0
0.1
0.2
0.3
0.5
1.0
LiCl
KCl
Concentration of Salt. (gm. equiv. per litre.).

Fig. 12.

SOL D.

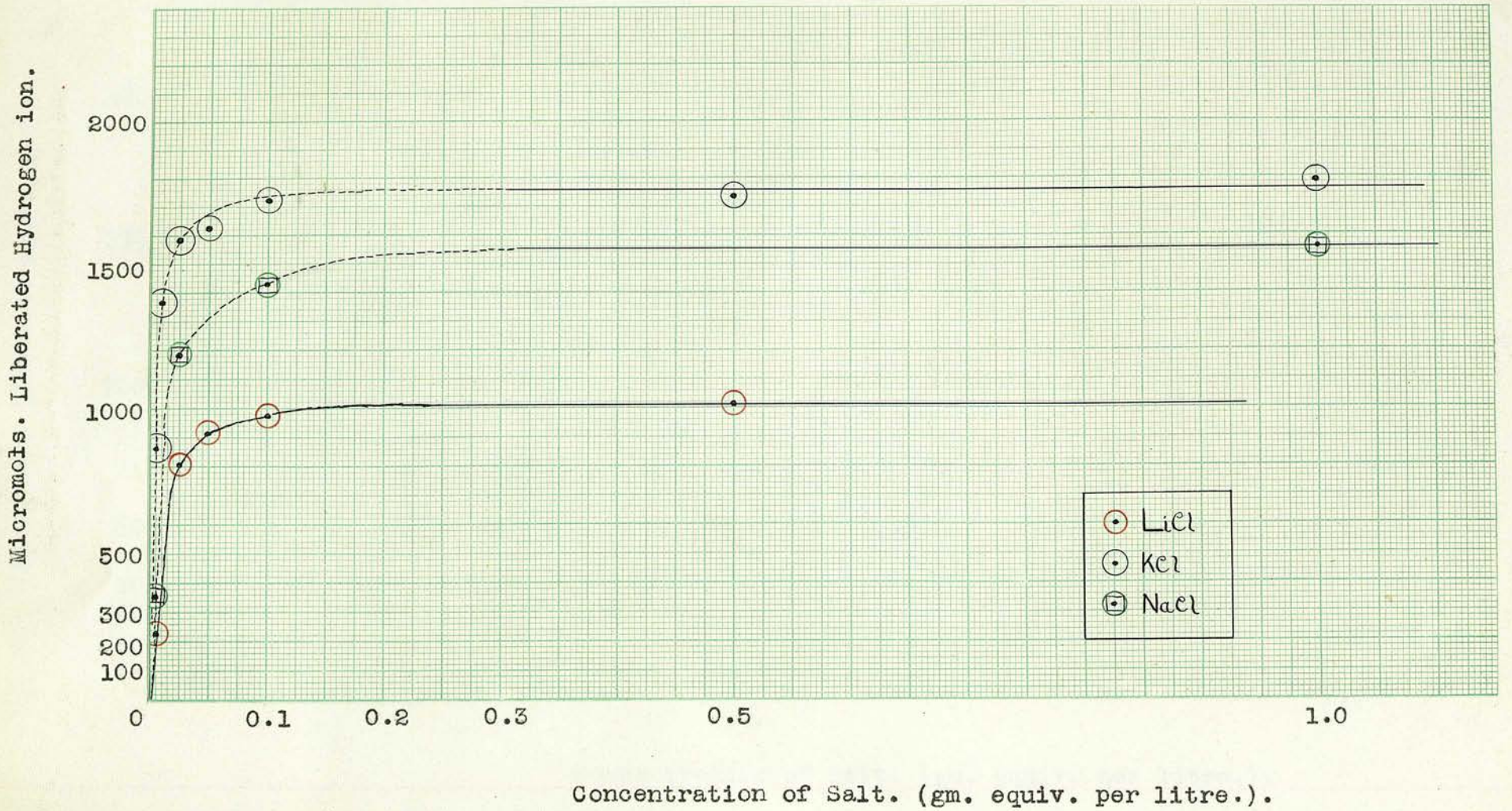
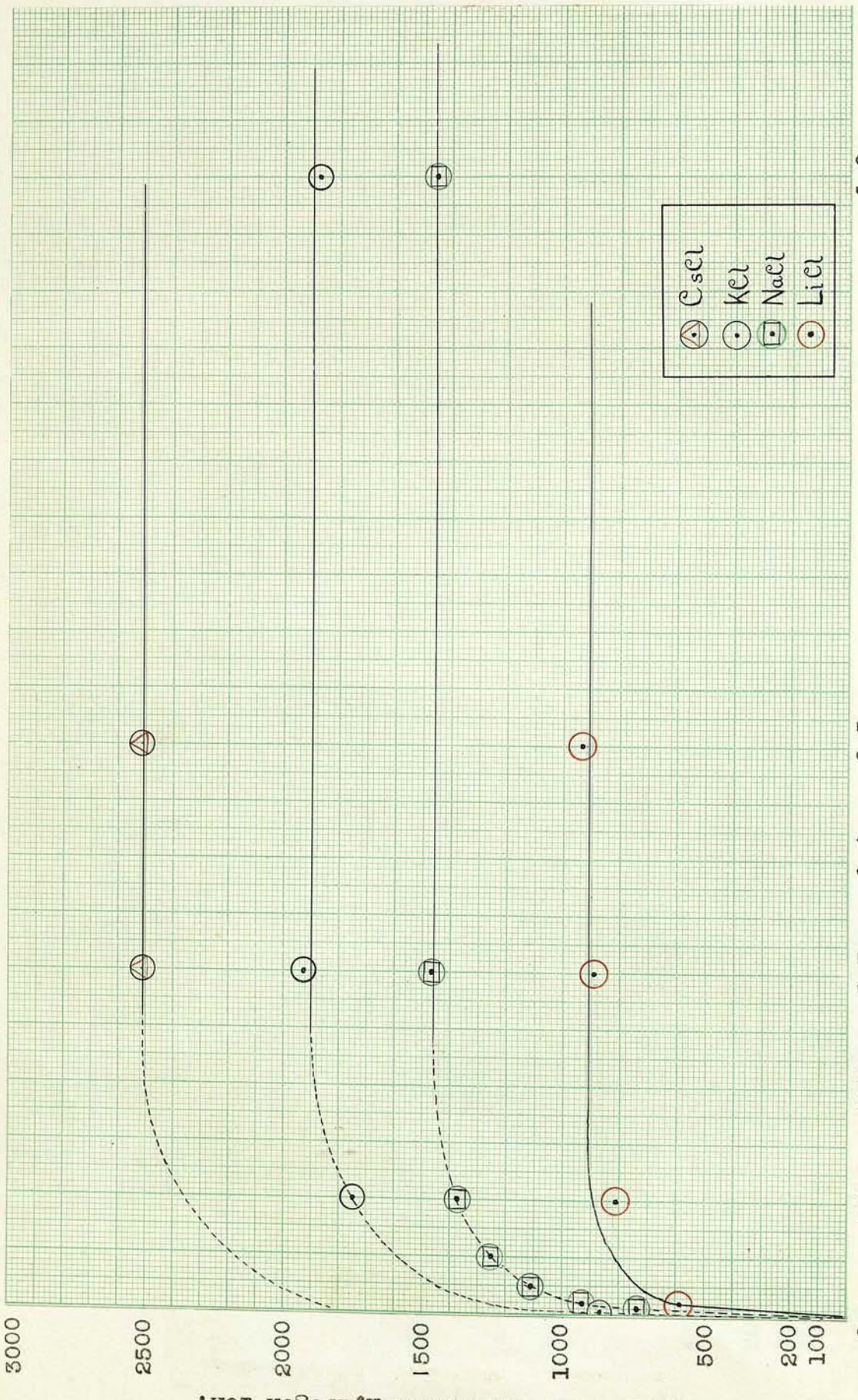

Micromols. Liberated Hydrogen ion.
2000
1500
1000
500
300
200
100
0
0.1
0.2
0.3
0.5
1.0
LiCl
KCl
NaCl
Concentration of Salt. (gm. equiv. per litre.).

Fig. 13.

Fig. 14.


SOL E.
Micromols. Liberated Hydrogen ion.
3000
2500
2000
1500
1000
500
200
100
0
0.1
0.2
0.3
0.4
0.5
1.0
CsCl
KCl
NaCl
LiCl
Concentration of Salt. (gm. equiv. per litre.).

explanation is that this portion of the added acid reacted with the ferric hydroxide present in the particles (as the result of hydrolysis) to reform prussian blue.

The constancy in the concentration of intermicellar acid attained in Sols C, D and E at some time or other after completion of dialysis, shows that an equilibrium was reached and that the sols were chemically stable. This agrees with the observation of Weiser and Milligan (loc. cit.) that hydroferrocyanic acid is stable when adsorbed on cupric ferrocyanide.

Liberation of Acid by Salts.

The data for the liberation of acid from the micelles of undialysed sols by the action of salts of the alkali metals (Table XIV - XIX) was plotted in figs.12,13 and 14. It will be seen that (1) in the case of any one salt, the amount of acid liberated increases with increase in the concentration of salt, to a maximum value,* (2) this maximum varies from salt to salt, (3) the order of increasing maximum value is Li < Na < K < Cs. This state of affairs was quite unexpected. If the increase in acidity of the intermicellar liquid is due simply to replacement, by the salt cations, of the hydrogen ions pertaining to the adsorbed/

* Indicated by continuous lines in figures. In Tables VII-XIX and Fig.12-14, the liberated acid in the case of Sol E is calculated by taking the intermicellar acid as having the earlier value of 14 m.e./l.(Table XIII, p.56)

adsorbed hydroferrocyanic acid, it would be anticipated that the maximum amount of acid liberated would be the same for every salt, and equal to the total amount of adsorbed acid. The investigations on ionic interchange in sulphur and other sols (see p.7) show, indeed, that this is the normal behaviour.

It might be thought that the exceptional behaviour of colloidal prussian blue is due to some peculiarity of the adsorbed hydroferrocyanic acid e.g. incomplete dissociation, so that the interchange itself is abnormal. Comparison of Sol F with Sol E , however, definitely disposes of this explanation, as the data in the following table show.

TABLE XXVIII.

Salt	Maximum amount of acid liberated.		Difference	Mean Difference
	Sol E *	Sol F x		
LiCl	704	956	252	
NaCl	1235	1472	237	
KCl	1665	1932	267	
$MgCl_2$	1113	1332	219	244

* Values obtained by subtracting later value for concentration of intermicellar acid (240 m.e./l ; Table XIII, p. 56) from values for 'total' acid given in Table XXI.

x Values from Table XXIII, p. 65 .

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* Values obtained by subtracting later value for concentration of intermicellar acid (240 m.e./l ; Table XIII, p.56) from values for 'total' acid given in Table XXI.

x Values from Table XXIII, p.65 .

It will be seen that, within the experimental error, the maximum amount of liberated acid increases by the same amount in the case of all four salts. The only reasonable conclusion is that the whole of the extra adsorbed hydroferrocyanic acid (amounting to 244 m.e./l. in Sol F) is replaced in the normal fashion, i.e. irrespective of the nature of the salt.

A probable explanation of the relations which exist in the case of prussian blue is that acid is liberated by some process, or processes, in addition to ionic interchange (as defined in the Introduction). One feature of the results which supports this view is revealed by comparing the maximum amounts of liberated acid for the different Sols.

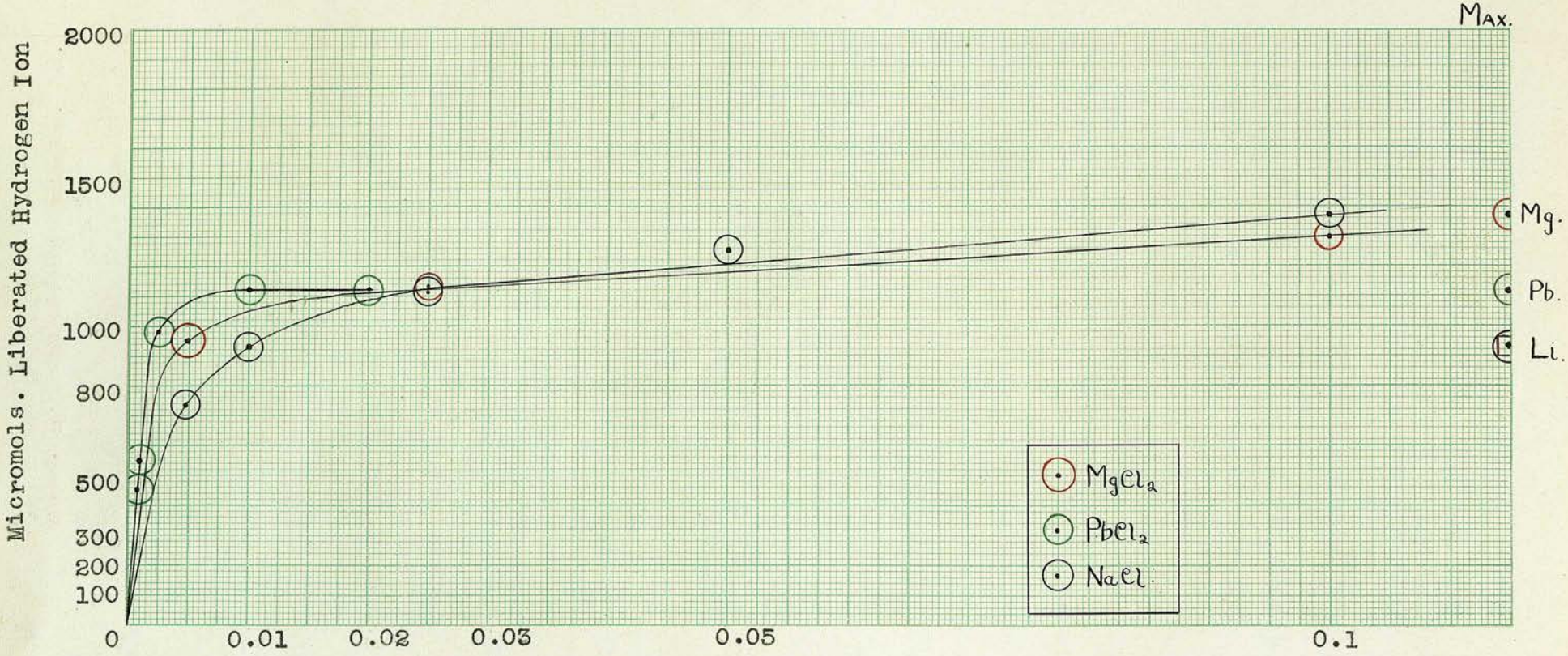
TABLE XXIX.

Salt	Maximum amount of acid liberated.*			Ratio $\frac{D}{E}$
	Sol C.	Sol D	Sol E	
LiCl	950	1015	704	1.44
NaCl	-	1555	1235	1.26
KCl	1860	1785	1665	1.07

* See Tables XIV, XV, XVI, and XXVIII.

As Table XXIX shows, the percentage decrease in liberated acid observed in going from Sol C or Sol D to Sol/

SOL E.



Concentration of Salt. (-gm. equiv. per litre.).

Fig. 15.

Sol E is much greater in the case of lithium chloride, than in the case of potassium chloride; sodium chloride being intermediate in behaviour. This is explicable on the assumptions that lithium ion liberates hydrogen ion by ionic interchange only and that some other action is superposed upon this process when other cations are employed.*

The data for magnesium chloride and lead chloride in the case of Sol E (Tables XVIII, XX) are plotted in Fig. 15 .x It will be seen that both salts liberate larger amounts of acid than does lithium chloride. in the case of Sol E after ageing (i.e. intermicellar acid = 240 m.e./l.) the maximum amount of acid liberated is the same for both salts - 1113 m.e./l. for magnesium (Table XVIII) and 1120 m.e./l. for lead (Table XX). Also the ratio

$$\frac{\text{maximum acid liberated in Sol D}}{\text{maximum acid liberated in Sol E}}$$

has practically the same value for lithium and magnesium - for lithium = 1.44 m.e./l. (Table VIII); for magnesium = 1.50 m.e./l. ($\frac{1665}{1113}$)

* Owing to this complication, dotted lines are used in Figs. 12 to 14 for the lower concentrations of salts, as indicating that the graph represents only the general trend of the data.

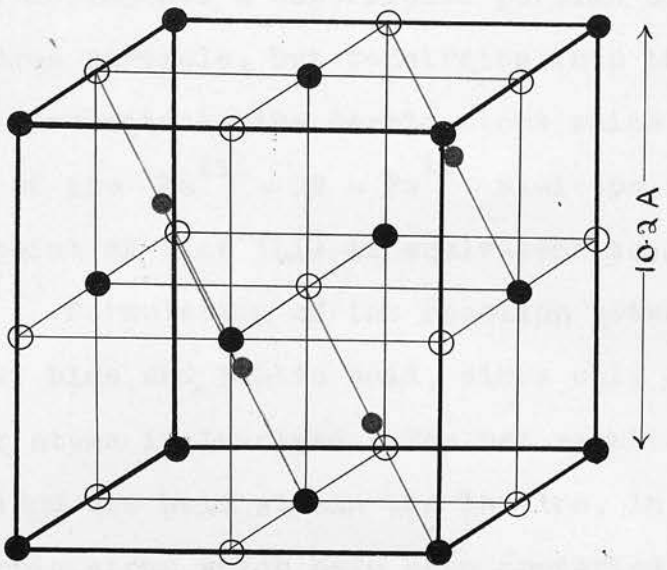
x The concentration of intermicellar acid is taken as 14 m.e./l. for $MgCl_2$, and 240 m.e./l. for $PbCl_2$.
Note:- In general the use of one or other of these values depends on the dates at which the particular determinations were made.

Nature of Special Processes.

Without further investigation, it is hardly possible to arrive at definite conclusions with regard to the nature of the processes which complicate the measurement of the normal ionic interchange in these prussian blue sols. Certain suggestions, however, may be put forward, as being at least consistent with the results as they stand.

Keggin and Miles[1] recently published a preliminary report on an important X-ray investigation of the crystal structure of the prussian blues. By the oxidation of compounds having the general formula $Fe^{ii}R_2\,Fe^{ii}(CN)_6$, where R = alkali metal or ammonium, prussian blues of general formula $Fe^{iii}\,R\,Fe^{ii}(CN)_6$ were obtained. The crystal structure of these compounds is found to be cubic, the iron atoms being arranged ferrous and ferric alternately, at the corners of cubes, in the edges of which lie the CN groups. The alkali metal atoms occur at the centres of alternate cubes as shown in the accompanying diagram.

(1) Keggin and Miles, Nature, 137, 577, (1936).



● Ferric

○ Ferrous

● Alkali metal

Keggin and Miles further state that, "blues containing no alkali have been prepared, and X-ray photographs show that the Fe-CN skeleton structure is cubic and similar to that already described. Here it seems that the additional iron, or iron in combination with a negative ion, can replace the alkali metal".

While proof is lacking that the 'insoluble' blue used in the present work is identical with the 'alkali-free' blue of Keggin and Miles, it seems very likely that one of every four ferric atoms will be differentiated in a similar manner. In respect to the present problem, therefore, it is suggested that in the/

the preparation of the sols the oxalic acid not only completely decomposes a superficial portion of the prussian blue particle, but penetrates into the particle and there attacks the ferric atoms which do not form part of the $Fe^{iii} - CN - Fe^{ii}$ skeleton. From a chemical point of view this is equivalent to Justin-Mueller's[1] formulation of the reaction between 'insoluble' blue and oxalic acid, since only one of every four atoms is involved. The net result is that hydrogen ions are held within the lattice, in place of the ferric atoms which have been converted to ferric oxalate.

It would appear that these hydrogen ions may be replaced by the cations of an added salt to a degree which depends upon the concentration of the salt and the nature of the cation. For salts of the alkali metals the order of decreasing replacing power is Cs > K > Na > (Li). According to the view previously advanced (p. 84) lithium ions take part only in normal ionic exchange, i.e., they will not displace hydrogen ions from the lattice at all.

The results of the analyses of coagula produced by the action of salts on undialysed sols are of importance/

(1) See p. 71.

importance in this connection. It will be seen from Table IV (p. 36) that the residue obtained on ignition of the coagulum contained alkali, to an extent depending upon the nature of the salt kation*. This alkali must arise from the decomposition of alkali metal ferrocyanide produced by the displacement of hydrogen from (1) adsorbed hydroferrocyanic acid (normal interchange), and (2) $HFe^{iii}Fe^{ii}(CN)_6$ present in the interior of the particles.

The amounts of alkali are in at least qualitative agreement with the determinations of liberated acid in so far that both give the same order of replacement - K > Na > Li . An exact comparison is not feasible since the intermicellar liquid of the undialysed sols. contained about 0.2N oxalic acid. This would undoubtedly tend to depress the normal ionic interchange, as happens, for example in the case of sulphur sols(1), the effect being greater in the case of lithium than in the case of potassium. However increase in acidity would/

(1) Bolam and Muir, J.C.S., 1022, (1933).

* In the case of lithium sulphate, if the ignition was carried out in a platinum vessel (Table IV , Li_2SO_4(1)), a yellow-green residue with a slightly acid reaction was obtained. This is in accordance with the experience of Jaeger and Klooster(1) who showed that interaction with the platinum occurs. However when pyrex vessels were employed for the ignition a small but appreciable alkaline residue remained (Table IV , Li_2SO_4 (2) and (3)).

(1)Jaeger and Klooster, Proc. R. Acad. Amsterdam, 16, 858, (1913).

would not influence the interchange to the extent necessary to account for the fact that about 100 times as much potassium as lithium was taken up by the micelles, (Table IV ; K = 0.2052 milliequivalents, Li = 0.003 milliequivalents). in the case of Sol A , while in the case of the dialysed sols the amount of acid liberated by potassium was only about twice that liberated by lithium. The conclusion is that lithium has little, if any, tendency to enter the lattice of the prussian blue micelle.

The work of Keggin and Miles (loc. cit.) seems to have a bearing on this point, since it was found that while oxidation of $Fe^{ii}R_2Fe^{ii}(CN)_6$ gave $Fe^{iii}R\,Fe^{ii}(CN)_6$ when R was potassium or sodium, the corresponding lithium compound was not obtained, the lithium being removed altogether*.

The origin of the differences in the extent to which different ions displace hydrogen from the interior of the particles is obscure. It may be that hydration is a factor, since the lithium ion is generally regarded as the most heavily hydrated in the alkali metal series.

The analyses of the coagula produced by the action of potassium chloride in Sol B (Table V and Fig.5.) showed/

* Keggin and Miles (private communication) also found that $Fe^{iii}Cs\,Fe^{ii}(CN)_6$ could not be obtained by oxidation of $Fe^{ii}CS_2Fe^{ii}(CN)_6$, but, on the other hand, the caesium was not completely removed from the lattice.

showed that displacement of hydrogen ion was not complete at 0.5 N salt, as happened with the dialysed sols. This must be connected with the fact that the amount of replaceable acid is much greater - 11392 m.e./l. ($0.5696 \times 1000 \times \frac{1000}{50}$) for Sol B , as compared with 1876 m.e./l. for Sol E. Dialysis in some manner, decreases the amount of acid present in the interior of the particles. Hydrolysis of the prussian blue would partially account for the change but there is also the possibility that a quantity of oxalic acid may be present within the micelles of the undialysed sols, which diffuses out during dialysis.

Ionic Interchange and the Mechanism of Coagulation.

Under the conditions of the coagulation experiments (pages - 66, 67), the bulk of the prussian blue was completely sedimented by the action of the centrifuge within 30 minutes from the time of adding the coagulant. The supernatant liquid had the appearance of an extremely dilute sol and underwent no visible change when allowed to stand for several hours, provided it was not exposed to the light. If, however, coagulant in sufficiently high concentration, was added to the supernatant liquid, the formation of aggregates could be easily observed. Moreover as will be seen from/

from the data in Tables XXIV, XXV, XXVI, the amount of prussian blue in the supernatant liquid, though very small, varied quite definitely with the concentration of salt used in the first instance. These factors suggest that prussian blue shows the phenomenon of 'fractional' coagulation, previously encountered in Sulphur[1] and Stearic acid[2] sols. The 'coagulation values' obtained in the present work are therefore those concentrations of the various salts which produced rapid coagulation of a certain large but definite fraction of the particles in the sol.

One point should be mentioned in connection with the actual determinations of the coagulation values. It was found that the intensity of coloration of the supernatant liquid (obtained by centrifugal action) depended very much upon the vigour with which the mixture of sol and salt solution was shaken and the duration of the shaking. Care was taken to standardise the conditions as far as possible and it will be seen from the reproducibility of the photometric figures that a sufficient degree of control was actually attained. It was observed that when the period of shaking/

(1) Bolam and Muir, loc. cit.

(2) Bolam and Duncan, loc. cit.

shaking was prolonged by two or three minutes, the colour intensity increased. Since the bulk of the coagulated blue tended to form a loose gel-like structure, it seems likely that uncoagulated particles would tend to be mechanically held by the coagulum and carried down by it. Shaking would break up the coagulum and liberate the enclosed uncoagulated colloid to a degree depending upon the violence and duration of the agitation.

Inspection of the coagulation data as a whole shows that the error in the determination of the coagulation values, as defined above, cannot be more than 3 per cent. The coagulation values are reproduced in Table XXX, together with the amounts of hydrogen ion liberated by these concentrations of the different salts (see also Table XXII). In most cases two independent determinations were made of the liberation of acid, with an interval of one to seven weeks between. The amount of hydrogen ion displaced was substantially constant, another indication of the chemical stability of the sols.

TABLE XXX./

TABLE XXX.

Sol E.

Salt.	Coagulation Value (equivalents per litre)	Acid liberated* at coagulation point (micromols per litre)
LiCl	0.011	358
NaCl	0.0047	510
KCl	0.003	616
$MgCl_2$	0.00186	624
$PbCl_2$	0.00095	448

* These determinations were made after the inter-micellar acid had risen to 240 m.e./l.

At present it is not possible to estimate in any given case the exact contribution of each process to the observed liberation of hydrogen ion. Hence the data do not permit of a definite conclusion in regard to the amounts of hydrogen ion liberated by normal ionic interchange at the coagulation point. There are, however, certain features of the results which show that they are not inconsistent with the view that the same amount of hydrogen ion is displaced from the adsorbed hydroferrocyanic acid by the cations of the salts at their respective coagulation values. In the first/

adsorbed hydroferrocyanic acid (on the assumption that the normal interchange is the same as for lithium). This leaves 0.000352 equivalents per litre, which is able to produce only 0.000090 (0.000488 - 0.000358) equivalents of acid by some special process.

If it is assumed that lithium liberates hydrogen ion by ionic interchange only, it follows that the interchange at the coagulation point is only about 50 per cent complete ($\frac{358}{708}$) . This suggests that the surface hydroferrocyanic acid is about half dissociated, and is intermediate in behaviour between the surface polythionic acid in Sulphur sols(1), and the surface stearic acid in Stearic acid sols(2). In this connection it appears significant that the slope of the liberated acid curve for lithium chloride becomes markedly less steep in the region of the coagulation value, which means that the remaining hydrogen ion is much less easily displaced than the earlier portion.

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(1) Bolam and Muir, loc. cit.

(2) Bolam and Duncan, loc. cit.

SUMMARY.

(1) The action of the neutral salts in liberating hydrogen ions from the micelles in prussian blue sols has been investigated by means of (a) electrometric determination of the acidity of the intermicellar liquid and (b) analysis of the coagulum. In particular the influence of the nature and the concentration of the salt has been studied.

(2) It is shown that prussian blue sols exhibit abnormal behaviour, in that the maximum amount of acid liberated varies with the nature of the salt cation. The order of increasing maximum liberation is found to be Li < Na < K < Cs.

(3) The results support the hypothesis that, while in the case of lithium the acid is liberated by normal ionic interchange, in the case of the other alkali metals, additional acid is liberated from the interior of the micelles.

(4) The influence of the various salts upon the stability of the Sols has been examined and it is shown that the results as a whole are not inconsistent with the view that the amount of hydrogen/

hydrogen ion liberated at the coagulation point by normal ionic interchange is the same for all the salts.

(5) The importance of the study of ionic interchange for a general theory of coagulation is discussed.

(6) The 'peptisation' of prussian blue by oxalic acid has been investigated.

In conclusion, the author wishes to express his indebtedness to Dr T.R. Bolam for his helpful suggestions and advice during the course of this work.

This is to certify that Mr WILLIAM TAYLOR successfully sustained an oral examination on the subject matter of his thesis by a committee of the department. This examination was held in April of this year.

Members of
Committee.

20 May, 1937.